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FEASIBILITY STUDY FOR THE DEVELOPMENT OF A MULTIFUNCTIONAL EMISSION DETECTOR FOR NO, CO, AND SO2

Arthur D. Snyder, et al

Monsanto Research Corporation
Dayton, Ohio

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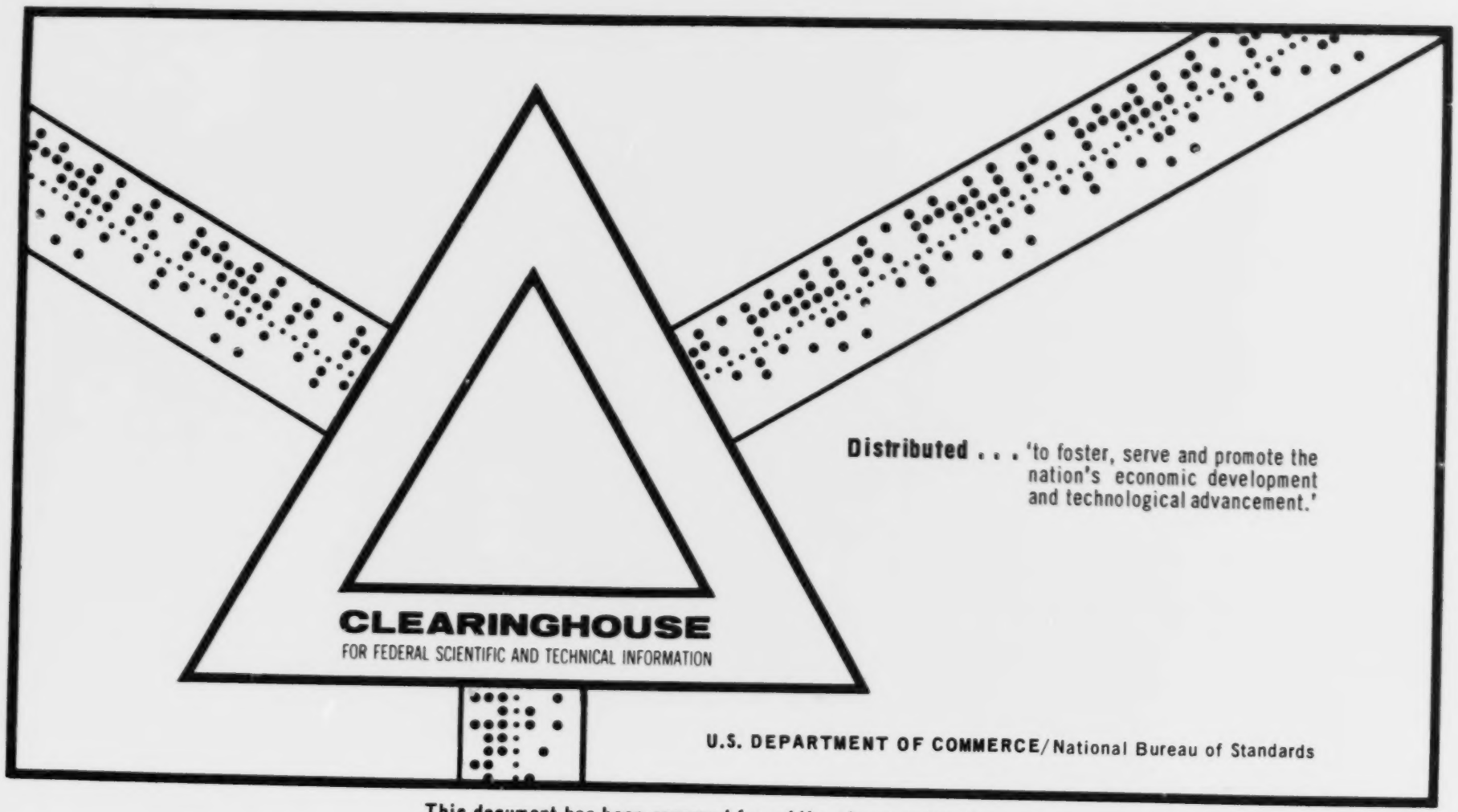
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Final Report

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George W. Wooten

For

National Air Pollution Control Administration
Chemical and Physical R & D Program
4676 Columbia Parkway
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Contract No. CPA 22–69–8

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ABSTRACT

The feasibility of multifunctional detection of NO, CO, and SO_2 in ambient air, based on the chemiluminescent reaction of these pollutants with atomic oxygen, was studied in a laboratory prototype detection system. Using this approach, concentrations as low as 5 ppb NO have been detected, and laboratory evidence predicts detection capabilities for SO_2 to be below 1 ppb. The CO-O reaction produced insufficient glow for adequate detection below approximately 100 ppm. A linear relationship was established between glow intensity and pollutant concentration in all cases. Nitrogen dioxide interfered with NO detection but no other serious interference problem was observed. Here, the responses of NO_2 and NO were identical, and the chemiluminescent reaction with atomic oxygen provides a sensitive means for detecting both NO and NO_2 in ppb concentrations. In both the NO_x-O and the SO_2-O reactions, the present detection limit characteristics of the laboratory apparatus can be significantly enhanced by further optimization of the system.

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1. INTRODUCTION

The complex nature of present day air pollution problems, with the attendant demands for more adequate and sensitive means for sampling and analyzing pollutant levels in the atmosphere, have given great impetus to the development of instrumentation capable of operating in a remote and continuous mode. Current literature is replete with work devoted to such ends. Many approaches and equally numerous instruments have been devised and assembled for detecting and analyzing small concentrations of NO, CO, and SO_2 in laboratory studies as well as in urban atmospheres. Despite advancements made thus far, the current state of development of continuous pollutant monitoring instrumentation leaves much to be desired and dramatizes the urgent requirements for further study in this area. Of paramount practical importance is the ultimate development of a sensitive, multifunctional detection system capable of analyzing minute concentrations of NO, CO, and SO_2 either sequentially or simultaneously.

Present monitoring instrumentation suffers from a wide variety of inadequacies. Most instruments are capable of monitoring only a single pollutant at a time; thus a large bank of instruments (if available) is usually needed to cover all the pollutants of interest. Many lack the sensitivity required to detect concentrations down into the parts-per-billion range, or are adversely affected by interfering components of polluted air, or both. Others display response times much too long for effective continuous monitoring. All, unfortunately, are so complex or so large and bulky as to be not generally applicable to large-scale sampling programs. The nonportable aspect is, obviously, a detriment to easy sampler dispersal. Instrument complexity demands that technically trained personnel operate the equipment.

This report describes a research study, the objective of which was to establish the feasibility of a continuous, multifunctional detection system based upon a novel application of present technology. The instrument concept depends upon the spectrophotometric analysis of the radiation emitted from chemiluminescent reactions of NO, CO and SO_2 with atomic oxygen. Since these reactions produce a characteristic glow, the detection principle shows great promise of being translated into a simple, highly sensitive instrument overcoming the many shortcomings of past instrumentation.

While beyond the scope of present program objectives, utilization of these chemiluminescent reactions in a simple, portable instrument design would, obviously, be the ultimate goal of this research.

2. SUMMARY

The feasibility of utilizing the chemiluminescent approach for detecting sub-ppm concentrations of NO, CO, and SO_2 was established by satisfying the following program objectives:

(1) Determining definitive spectral characteristics of the NO-O, CO-O, and SO_2-O chemiluminescent glows.

(2) Defining the approximate lower limits of detection for NO, CO, and SO_2 via chemiluminescent reactions.

(3) Determining the extent of interferences by other components common to polluted air (e.g., N_2O, CO_2, CH_3, H_2O, and NO_2).

(4) Fabricating a breadboard system to demonstrate the capabilities of the proposed detection system.

The technique employed for pollutant assessment was based upon the following simplified generalized reaction:

$$XO + O = XO_2 + h\nu$$

where X is either N, C, or S, and the intensity of the emitted radiation (I) is given by:

$$I = k(XO)(O)$$

where (XO) and (O) are the concentrations of the reacting species.

Atomic oxygen was produced by a microwave discharge through molecular oxygen. A constant atom concentration in large excess over the concentration of the pollutant(s) was maintained. Under these conditions the intensity of the chemiluminescent glow should increase monotonically with increasing pollutant concentration.

A breadboard prototype detection system was designed and fabricated for the laboratory feasibility study. This prototype consisted of a vacuum system, reaction chamber, microwave generator with associated powermeter and quarterwave cavity, and a dual detection system consisting of a 1.5-meter spectrograph or an optical filter-photomultiplier, amplifier, and recorder combination. The resulting detection flexibility allowed photographically recorded spectra of the chemiluminescent glows to be taken as well as glow intensity measurements to be made photometrically. In conjunction with the above apparatus, a metering and mixing

system was designed for delivering known pollutant concentrations in the low ppb range to the reaction chamber.

The chemiluminescent approach proved to be very successful in terms of NO and SO_2 detection but the CO-O reaction was too insensitive to provide adequate detection capability. As little as 5 ppb NO was detected in the laboratory system using a narrow bandpass filter with low (30%) transmission properties. A linear relationship was found to exist between glow intensity and concentration from 5 ppb to concentrations in excess of 3000 ppm. A regression analysis of all data indicated confidence limits for a least squares linear fit to exceed 99.5% in all cases. The deviation of the slopes of the intensity versus concentration curve for individual sets of data from an average value obtained by including all data was found to be less than 3%. An increased sensitivity was observed when the nitrogen diluent commonly used was replaced by argon. With nitrogen diluent, a sensitivity corresponding to 2.8×10^{-10} amperes/ppm NO was determined. A tenfold increase (2.8×10^{-9} amperes/ppm NO) was found with argon diluent.

The glow intensity resulting from the SO_2-O reaction also increased linearly with concentration. Initial intensity measurements made through a 50 A bandpass filter indicated that a lower detection limit of 100 ppb SO_2 might be the limiting sensitivity. Replacing this filter with one exhibiting much broader bandpass and higher transmission characteristics led to a conservative detection limit estimate approaching 1 ppb. In both the NO-O and the SO_2-O reactions, the 1 ppb lower limit of detection characteristic of the laboratory apparatus could be significantly reduced by further optimization of the system. Changes in reactor geometry and reactor-photomultiplier orientation would enhance the recorded emission intensity by increase in emitting volume and more optimum transfer of light onto the sensitive area of the detector.

Since the lower limits of detection for NO, and SO_2 by chemiluminescent reactions were established under very idealized conditions, a study of the effects (if any) of other polluted air constituents on detection sensitivity was required to assess the applicability of the chemiluminescent approach to practical monitoring problems. For the purpose of this program, five possible interfering components were studied: N_2O, CO_2, CH_3, H_2O, and NO_2.

Nitrogen dioxide was the only case where interference was observed to any real and measurable extent. Here, the response of NO_2 and NO is identical, both oxides showing linear glow intensity-concentration relationships and exhibiting identical

curve slopes. Spectra of the chemiluminescent glow resulting from the reaction of NO_2 and atomic oxygen further substantiate the similarity. The chemiluminescent reaction involving the oxygen atom is therefore not selective for NO alone but still provides a sensitive means for detecting NO-NO_2 in ppb concentrations.

3. CONCLUSIONS AND RECOMMENDATIONS

While it was not the objective of this program to finalize a design for an operating field instrument, the conclusions and recommendations resulting from the study indicate a strong feasibility of applying the chemiluminescent approach to real air monitoring needs. These conclusions and recommendations are listed below:

(1) The chemiluminescent reaction of NO_x and SO_2 with oxygen atoms can be used to independently determine these gases at a detection limit of about 1 ppb using the present laboratory apparatus. CO, on the other hand, did not exhibit sufficient chemiluminescent intensity to justify further consideration without a major optimization effort.

(2) The sensitivity and lower limit of detection of combined ($NO + NO_2$) and SO_2 are amenable to a very significant improvement by optimization of reactor design and improved orientation of the reactor-photomultiplier combination.

(3) Optimization of the reactor-detector combination would permit detection of the glows at much lower gains, permitting the use of simplified associated electronics.

(4) An alternate method for producing oxygen atoms other than microwave or electric discharge of molecular oxygen could substantially reduce background interference.

(5) Formation of oxygen atoms by the dissociation of ozone would result in a reactant stream with a much lower concentration of nitrogen oxide impurity.

(6) The chemiluminescent approach is recommended as a pollutant instrumentation concept for the multifunctional detection of both NO_x and SO_2 on either sequential or simultaneous, real time, and continuous basis.

(7) The chemiluminescent concept is amenable to engineering design, fabrication and qualification testing of a packaged, portable instrument.

(8) Other chemiluminescent approaches such as the reaction between ozone and NO to determine either pollutant in the presence of excess of the other pollutant could also merit consideration.

4. BACKGROUND

4.1 HISTORY OF THE CHEMILUMINESCENT APPROACH

A method of analysis of common pollutants is required that will quantitatively determine gases at very low concentrations in air. Nitric oxide (NO), carbon monoxide (CO), and sulfur dioxide (SO_2) can occur at concentrations as low as 10 parts per billion. The monitoring methods described in this report are based on the development of a continuous monitor for these gases, employing chemiluminescent reactions with atomic oxygen generated by microwave discharge. All of the monoxides (NO, SO, CO) undergo reactions with atomic oxygen to form a metastable dioxide in an excited electronic state. Emission from the metastable product occurs through a resonance transfer process. When the oxygen atom concentration (O) is held constant, the measured intensity of the reaction is directly proportional to the concentration of the oxide.

This section briefly discusses the history of the chemiluminescent reactions, including mechanisms and chemical kinetic considerations. It then presents the spectral characteristics of the chemiluminescent emissions. Finally, it discusses the ultimate sensitivity of the analysis procedure.

The chemiluminescent reactions in the nitrogen-oxygen system have received a great deal of attention and the mechanism of the reactions are well established. The behavior was first observed by Strutt (Ref. 1), who observed a continuum emission after electric discharges in air. The continuum was originally attributed to a reaction between ozone and nitric oxide and became known as the "air afterglow". Further studies (Refs. 2-8) of the spectral characteristics of individual N-O species were interpreted in terms of the direct, one-step chemiluminescent reaction (Ref. 8):

$$NO + O \rightarrow NO_2 + h\nu \qquad (1)$$

This mechanism was employed for quantitative analysis of either atomic oxygen or nitric oxide by a number of investigators (Refs. 9-14) who correlated the measured intensity of the emission to the product of the two reactant concentrations, (O) and (NO), in kinetic studies in flames and oxygen atom reactions at low pressure and room temperature. The reactions were widely employed for characterization of the upper atmosphere in both simulated laboratory studies (Refs. 15, 16) and in Aerobee XI-A rocket probing experiments using a nitric oxide payload at 106 Km (Ref. 17).

The detailed spectrographic study of Broida, et al. (Ref. 18) of the chemiluminescent reaction between nitric oxide and atomic oxygen indicated that the mechanism was more complex than reaction (1) would indicate. Broida proposed the following reaction scheme:

$$NO + O + M \rightarrow NO_2 + M \qquad (1')$$

$$NO + O + M \rightarrow NO_2^*(C) + M \qquad (2)$$

$$NO_2^*(C) + M \rightarrow NO + O + M \qquad (3)$$

$$NO_2^*(C) \rightarrow NO_2^*(B) \qquad (4)$$

$$NO_2^*(B) \rightarrow NO_2^*(C) \qquad (5)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (6)$$

$$NO_2^* + M \rightarrow NO_2 + M \qquad (7)$$

where * indicates the excited state, M is any third body, and $NO_2^*(B)$ and (C) are separate excited states, both of which can contribute to the emission observed in reaction (6). A steady-state treatment of the intensity resulting from this mechanism leads to the approximate expression:

$$I \sim 10^{-21} k_4 (NO)(O) \qquad (8)$$

which is in agreement with the earlier observed proportionality of intensity and product concentrations.

The same general behavior exhibited by NO has been observed in the cases of CO (Refs. 19, 20) and SO (Refs. 21, 22) on interaction with atomic oxygen. Although the detailed reaction mechanisms for these oxides have not been established, they are very likely complex. For this discussion, however, the reactions can be written in the simplified form:

$$XO + O \rightarrow XO_2 + h\nu \qquad (9)$$

where X can be N, C, or S. The intensity, I, of the reaction has been shown to be proportional to the products of the reactant concentrations:

$$I = k(T)[XO][O] \qquad (10)$$

where k(T) is the temperature-dependent rate constant leading to the emitted radiation. Equations (9) and (10) are, therefore, the basis of the proposed analyses for all three oxides. In the

case of SO_2, interaction with atomic oxygen yields a stoichiometric concentration of SO, which is the source of the chemiluminescent behavior. When the oxygen atom concentration is maintained at a value in large excess over the monoxide concentration, the intensity should be a linear function of pollutant concentration.

4.2 CHEMICAL KINETIC CONSIDERATIONS

Two problems that must be considered in applying the chemiluminescent reactions to a practical field-monitoring analytical instrument are (1) quenching of the chemiluminescent emission and (2) kinetic interference by other species normally samples in air. Both interferences can be considered to be quenching processes; the first is physical in nature and the second is of chemical origin.

Classical quenching processes occur by collisional transfer of energy from the excited species to a third body, M, as follows:

$$XO_2^* + M \rightarrow XO_2 + M \qquad (11)$$

The extent of this process is a function of the number of collisions that can occur during the radiative lifetime of the excited state and the quenching efficiency or quenching cross-sections of the third body (Ref. 23).

Kaufman (Ref. 24) has shown that the light intensity from the NO-O reaction near the mixing region is independent of the nature and concentration of added gases such as Ar, N_2, CO_2, H_2, N_2O, etc. The nature of the light emission is sufficiently constant that Kaufman (Ref. 13) used the NO-O chemiluminescent system as an analytical tool for studies of the rates of the reaction of a wide variety of gases with atomic oxygen. This technique is often referred to as a gas-phase "titration". The rates of reaction of NO, O_2, SO_2, N_2, Ar, CO_2, H_2, CO, N_2O, C_6H_6, SO_3, $Fe(CO)_5$, H_2O, O_3, C_2H_5, Cl_2, and Br_2 with atomic oxygen were calculated from the measured decay rate of the chemiluminescent intensity immediately after mixing and further downstream in a glass tube. The rate of change of intensity in the system is equal to the rate of decrease in oxygen atom concentration. These results indicate that, for a wide range of possible "foreign" gases in polluted air, the quenching of the NO-O chemiluminescence is <u>not</u> a critical problem.

The second source of interference that could be encountered is chemical in nature. Since the concentration of oxygen atoms employed in the proposed study would be large compared to the pollutant being analyzed, chemical reaction of "foreign" gases

with oxygen atoms (such as above) would not be a critical factor. The intensity would be directly proportional to the concentration of the pollutant (NO, CO, SO_2). The problem of chemical "quenching" therefore is limited to species present in sampled air that would react with NO, CO, or SO. This reaction rate must be rapid so as to compete with the chemiluminescent reaction rate. SO (the active species for SO_2 analysis) and NO are both highly reactive. The use of nitric oxide as a hydrocarbon free radical scavenger is well-known (Ref. 25).

$$R\cdot + NO \rightarrow RNO \qquad (14)$$

where R is any hydrocarbon radical. Under the conditions downstream of the microwave discharge, the hydrocarbon gases sampled in the air could undergo dehydrogenation to form the free radical and might be a potential source for decrease in intensity of the chemiluminescence. Kaufman's (Ref. 13) studies, however, were conducted with microwave generation of atomic oxygen, and the presence of benzene and ethylene in mixtures with nitric oxide did not cause any measurable effect on the intensity. Based upon these results, the chemical "quenching" of the atomic oxygen chemiluminescent reactions does not appear to be a problem.

4.3 SPECTRAL CHARACTERISTICS AND SENSITIVITY

Successful use of these chemiluminescent reactions in the design of a multifunctional detection approach depends largely on the spectral characteristics of the chemiluminescent glows produced and on the detection sensitivity. The spectral distribution of each glow, obviously, must be sufficiently different from one another if the various pollutants of interest are to be distinguished. Sensitivity, likewise, must be such that the radiant intensity of the glow resulting from pollutant concentrations as low as a few parts per billion is substantially above the equivalent noise input of the detector(s) employed.

Spectral data taken from the literature indicate that the first requirement should be easily met. The chemiluminescent glow of NO and SO_2 with atomic oxygen is characteristically "continuous" in nature, with some indication of very diffused banded structures attributed to polyatomic molecules. Clyne and Thrush (Ref. 19) determined the spectral distribution of NO-O and CO-O chemiluminescent glows and measured absolute emission intensities. The NO-O emission is typically yellow-green in appearance; the radiant energy extends from above approximately 4000 A into the infrared. The greatest portion of this energy, however, is distributed around a maximum at 6500 A. The maximum

intensity of the CO-O emission was determined and found to occur at 4000 A, extending from below 3000 A to above 5000 A. Halstead and Thrush (Ref. 22) studied the chemiluminescent reaction of SO-O and report a "continuous" emission from approximately 2400 A to above 3800 A, with the maximum occurring at 2700 A. The three maxima, 6500 A, 4000 A, and 2700 A, are amply separated and should provide for positive identification and assessment of NO, CO, and SO_2 when appropriate filter-detector combinations are employed. Inasmuch, however, as the spectral characteristics of these glows are influenced to varying degrees by such parameters as pressure, etc., a laboratory verification of the reported results was required under the conditions of our studies.

Whereas considerable information is found in the literature with respect to NO-O, CO-O, and SO_2-O spectra, very little information was found that is pertinent to defining the ultimate sensitivity of the method. This is due, in part, to the fact that minimal effort was expended in optimizing the systems employed, especially with respect to detection. In most instances, the investigator was not interested in this aspect of the problem and consequently worked with larger concentrations of NO, CO, and SO_2 than were considered in our study. Despite this lack of direct information, however, a knowledgeable forecase of sensitivity can be made. This forecast, based on the performance characteristics of commercially available selected photomultiplier detectors, would predict detection of extremely low concentrations. These detectors are capable of counting single photons, and when employed in an optimized reaction system, should easily detect pollutants in the desired concentration range.

The sensitivity of the chemiluminescent approach for analysis of NO, CO, and SO can be estimated from the known sensitivities of phototubes and from the quantum yield of the reactions with oxygen atoms. The equivalent noise input into a 1P21 phototube ranges from 5×10^{-13} to 1.3×10^{-12} lumen. One lumen (5550 A) is equivalent to 1.47×10^{-3} watts or 1.47×10^{4} ergs/sec. The quantum energy for 5550 A radiation is

$$\varepsilon = h \frac{c}{\lambda} = 3.58 \times 10^{-12} \text{ erg/quantum} \qquad (13)$$

Therefore, 1 lumen (5550 A) = 4.1×10^{15} quanta/sec. The noise input to the phototube therefore ranges from 2.05×10^{3} to 5.3×10^{3} quanta/sec, and for accurate analyses by chemiluminescent detection, a radiant flux of about 4×10^{5} quanta/sec is required.

Kaufman (Ref. 13) has measured the quantum yield of the NO-O reaction as an average quantum (5550 A) being emitted for every 10^7 collision of O with NO. The radiant flux from the reaction can be calculated by consideration of the bimolecular collision rate:

$$Z_{NO-O} = \left(\frac{8\pi kT}{\mu}\right)^{1/2} \sigma^2_{NO-O} n_{NO} n_O \qquad (14)$$

where: Z_{NO-O} = collisions/cc sec between NO and O

k = Boltzman's constant = 8.314×10^7 erg/°K

T = temperature, °K

μ = reduced mass = $\frac{m_{NO} m_O}{m_{NO} + m_O}$

σ_{NO-O} = average collision diameter, cm = $\frac{\sigma_{NO} + \sigma_O}{2}$

n_O, n_{NO} = concentration in particles/cc

The collision rate was calculated for a reactant volume of 1 cm^3, a total pressure of 5 mm Hg, and a temperature of 300°K. An oxygen flow rate of 150 micromole/sec was assumed with 50% dissociation to atomic oxygen in the microwave cavity. The air sampling flow rate was set at A moles/sec and the concentration of NO in the air was set at (X) parts per billion.

At 5 mm Hg and 300°K the total concentration of all species is 1.6×10^{17} molecules/cc (Loschmidt's number corrected for temperature and pressure). Since the total flow including undissociated and dissociated oxygen is $(A + 2.25 \times 10^{-4})$ moles/cc:

$$n_O = \left(\frac{1.5 \times 10^{-4}}{A + 2.25 \times 10^{-4}}\right) 1.6 \times 10^{17} \qquad (15)$$

$$n_{NO} = \left(\frac{10^{-9} A(X)}{A + 2.25 \times 10^{-4}}\right) 1.6 \times 10^{17} \qquad (16)$$

Using these values the collision frequency of NO and O is:

$$Z_{NO-O} = \frac{6.83 \times 10^{11} A(X)}{(A + 2.25 \times 10^{-4})^2} \qquad (17)$$

and from Kaufman's quantum yield the quantum emission rate is

$$I = 10^{-7} Z_{NO-O} = \frac{6.83 \times 10^{4} A(X)}{(A + 2.25 \times 10^{-4})^{2}} \qquad (18)$$

This value must exceed 4×10^{5} quanta/sec for accurate analysis employing phototubes. At an air sampling rate of 100 micromoles/sec

$$I = 6.47 \times 10^{7}(X) \geq 4 \times 10^{5} \text{ quanta/sec} \qquad (19)$$

The lower accurate analysis limit (100% of photomultiplier noise level) is therefore equivalent to an NO concentration of about 10^{-2} parts per billion in air.

This value represents an ideal theoretical limiting sensitivity and does not include emission losses due to third body quenching, competitive reactions with interfering gaseous species, and the practical optical problem of delivering the emitted radiation to the phototube element. The calculation does, however, indicate the potential of the chemiluminescent approach for analysis of minute quantities of NO pollutant.

The same general considerations have been applied to the sensitivity of the CO-O and SO-O analyses. Mahan and Solo (Ref. 26) have determined that the quantum yield of the CO-O reaction at 298°K is 1/350 based upon the number of CO_2 molecules produced. Calculation of the collision frequency employed in the experiments indicates that at 298°K:

$$Z_{CO-O} = 1.0 \times 10^{20} \text{ collisions/cc-sec} \qquad (20)$$

The rate constant for formation of CO_2 is given as 10^{-7} cc/mole-sec at 300°K. From the conditions of their experiments the rate of formation of CO_2 in molecules/cc-sec is calculated to be 9×10^{12}. The number of collisions required for emission of one quantum is therefore $\frac{1.0 \times 10^{20}(350)}{9 \times 10^{12}}$, or about 4×10^{9} collisions. This implies that the intensity from the CO-O reaction would be about 400 times less than that for the NO-O reaction. Clyne and Thrush (Ref. 19) have compared the absolute intensities of the two reactions and find the NO-O reaction is 5000 to 2000 times more intense than the CO-O reaction depending upon whether argon or oxygen is the major third body. The theoretical lower limit of detection (100 x noise level) for CO using the factor of 5000 would correspond to about 5 parts per billion.

Recently Halstead and Thrush (Ref. 27) have measured the absolute intensity of the sulfur dioxide afterglow to be about 9 times more intense than the air afterglow. The intensities of the air and SO afterglows are given by

$$I_{air} = I_{oa}\,[O][NO] \tag{21}$$

$$I_{SO_2} = I_{os}\,[O][SO] \tag{22}$$

The ratio of the constant is $I_{os}/I_{oa} = 1.5 \times 10^{8}/4 \times 10^{7} \cong 4$. The intensity from the SO-O reaction is therefore greater than from the NO-O reaction and should result in limiting sensitivities near 10^{-3} parts per billion of SO_2 in air.

5. LABORATORY FACILITY FOR STUDYING CHEMILUMINESCENT REACTIONS

5.1 GENERAL REQUIREMENTS

A flexible laboratory facility was deemed essential for this study in order to achieve the rather diverse program objectives delineated in the contract. From the experimental point of view, two basic requirements were imposed. First, to facilitate spectral characterization of the various chemiluminescent reactions, fairly intense glows had to be produced if spectral data were to be taken photographically. To achieve this, the pollutant gas additive must be introduced into the reaction chamber in sufficient concentration to insure adequate intensity, thus permitting fairly short spectrographic exposures to be made. No attempt is made at this time, however, to determine the concentration of the additive. Conversely, the remainder of the program required photoelectric measurements to be made on faint chemiluminescent glows resulting from the addition of extremely small concentrations of the pollutants under study to the reaction chamber. Here, measured concentrations were required in order to establish intensity/pollutant concentration relationships, determine lower detection limits for each pollutant, and to study the effects of possible interfering gases. In addition, this facility also had to serve as our laboratory detection system for demonstrating the capability of the chemiluminescent detection approach. With these objectives and associated requirements in mind, considerable effort was directed in the early stages of the program to design and fabricate a functional laboratory apparatus which would best serve in satisfying all objectives of this study.

5.2 OPERATIONAL PRINCIPLE AND DESIGN CONCEPT OF EXPERIMENTAL APPARATUS

The operational principle on which the design of a chemiluminescent detection system is based is very simple and should provide (in theory at least) for rapid and sensitive assessment of NO, CO, and SO_2. Polluted air is introduced by a controlled and metered flow into a specially designed, low pressure reaction chamber, meeting a controlled and metered flow of atomic oxygen in a region optically aligned with a spectrograph, scanning spectrometer, or photomultiplier detectors; depending on the nature of the study. Oxygen atoms are produced by a microwave discharge through molecular oxygen. The chemiluminescent glow resulting from the reaction of atomic oxygen with NO, CO, and SO_2 is viewed through three band-pass filters that isolate a specific spectral band for each pollutant. The intensity of

the radiation passed by each filter is measured and recorded on a strip chart recorder. The intensity measured in each case is a function of pollutant concentration.

The design philosophy taken in this phase of the program was to employ commercially available components wherever possible in order that a flexible system could be fabricated at the earliest feasible time. Performance parameters of the components would in every instance be expected to exceed anticipated requirements to ensure acceptable operational capability over a wide range of conditions. The purchased components and items designed and fabricated in-house would be assembled in a "breadboard" configuration and used throughout the course of the study.

5.3 DESIGN AND FABRICATION OF EXPERIMENTAL APPARATUS

5.3.1 General

An experimental laboratory apparatus was designed, fabricated, and assembled along the lines discussed above to facilitate detailed studies of chemiluminescent glows resulting from the reaction of NO, CO, and SO_2 with atomic oxygen. A very preliminary laboratory detection system design was first assembled and studied for the purpose of establishing the salient design requirements which would lead to an optimal laboratory system. From this study, a better feel for reaction chamber design, gas flow rate and gas flow regulation requirements, pumping capacity, and power considerations, etc., was achieved and led to the design finally found acceptable for the program. A schematic diagram of the facility is shown in Figure 1. Basically, it consists of a vacuum system; reaction chamber; microwave generator with associated power meter and quarter-wave cavity for generating atomic oxygen; detection system, which ranges from optical filter/photomultiplier combinations with electronic read-out to photographic recording capabilities employing a 1.5-meter spectrograph; and a gas flow metering and mixing system required for metering, mixing, and delivering known concentrations of gas components to the reaction chamber. The various components comprising the facility are discussed separately below.

5.3.2 Vacuum System

The same vacuum system was used throughout the course of the study and consequently had to be considerably flexible in design to facilitate the different reactor designs and detection modes. Figures 2 and 3 provide an overall view of the facility set-up for spectrographic studies and show in some detail the vacuum arrangement employed. The reaction chamber, regardless of its

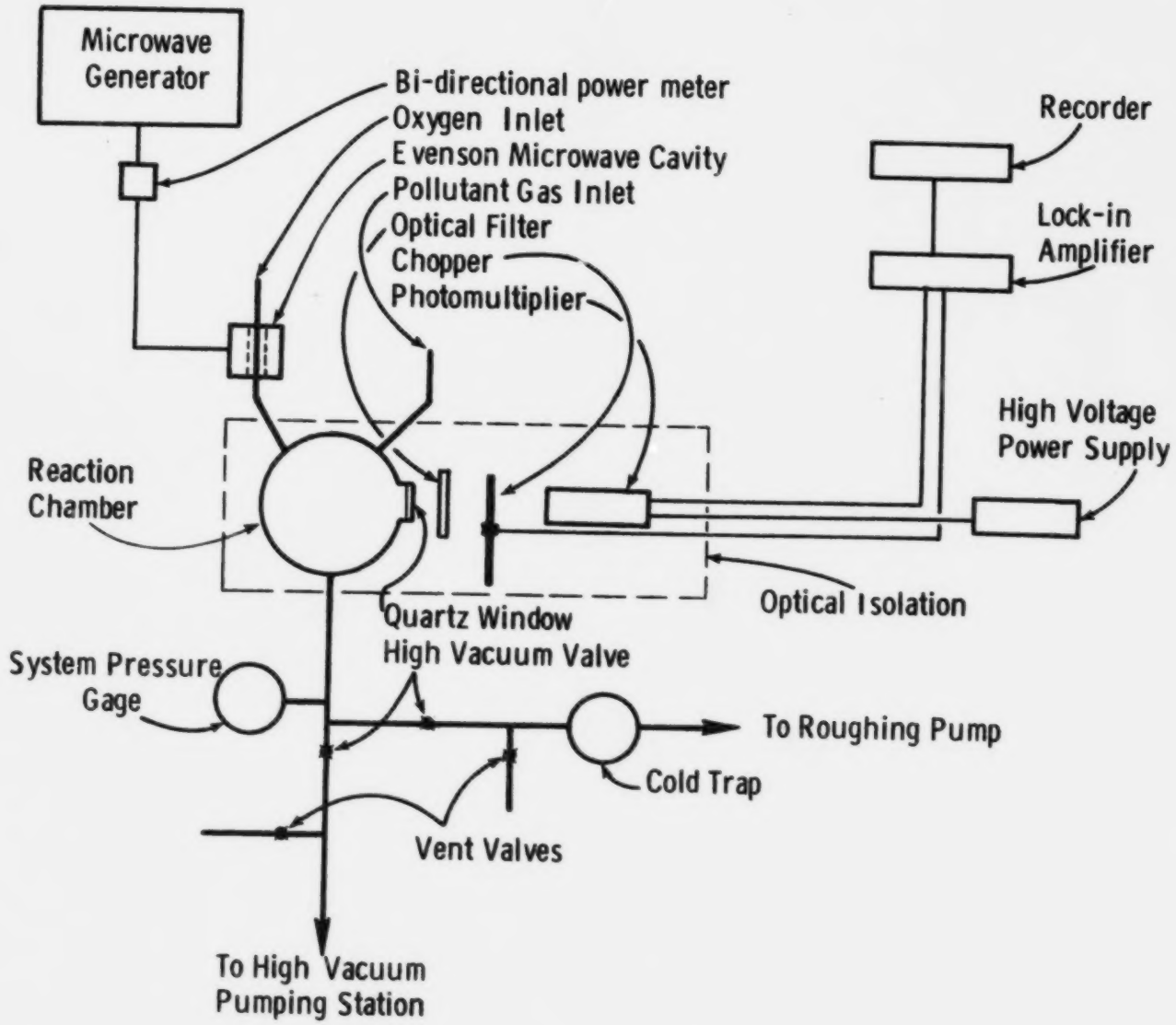


Figure 1. Schematic of Laboratory Detection System.

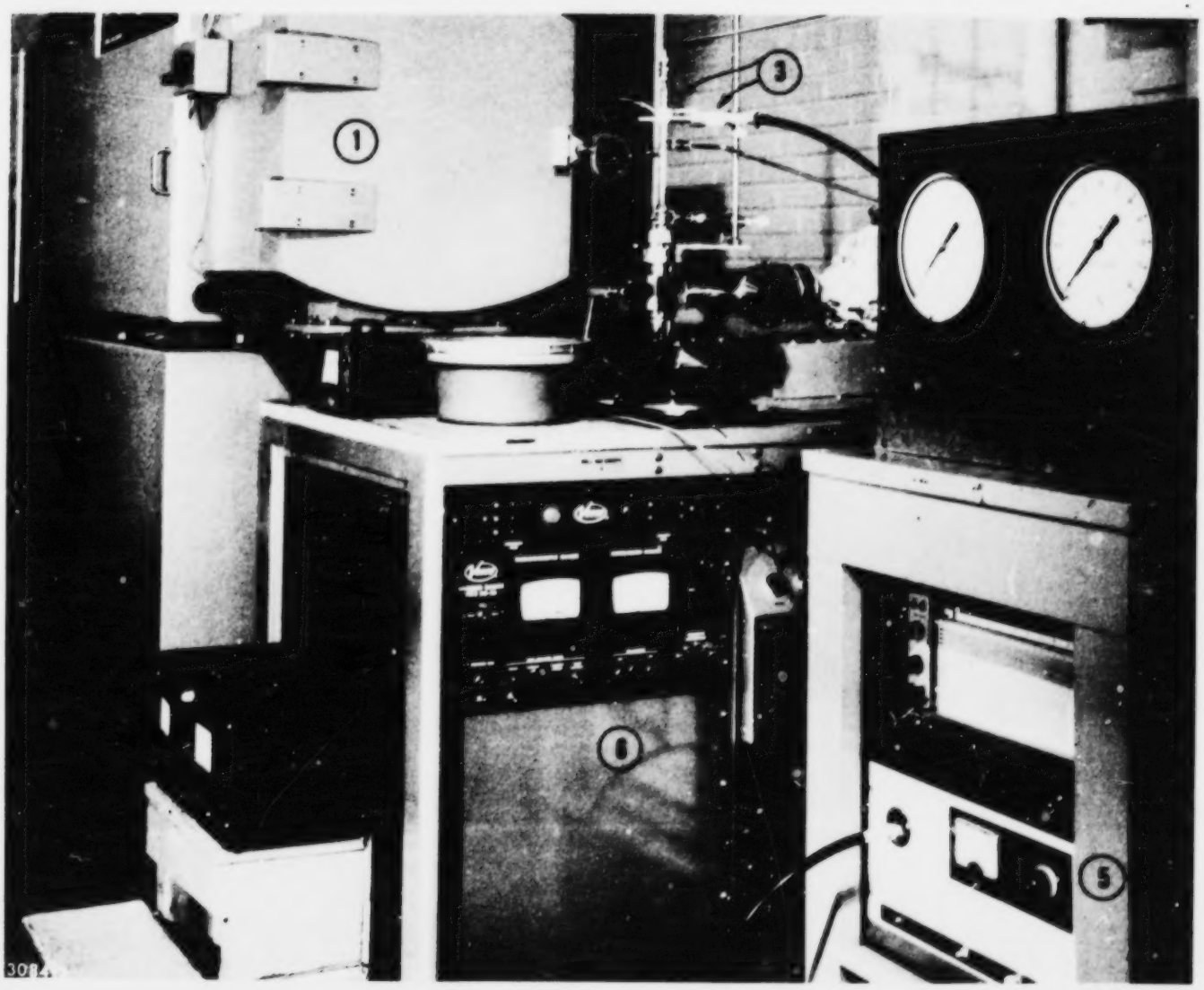


Figure 2. Laboratory Arrangement for Spectrographic Studies.

(1) Jarrell-Ash 1.5 Meter Plane Grating Spectrograph
(2) Spherical Quartz Lens
(3) Microwave Cavity-Reaction Chamber
(4) Gas Flow Metering and Mixing System
(5) Raytheon 100 watt 2450 MHz Microwave Generator
(6) Veeco Hi-Vacuum Pumping Station

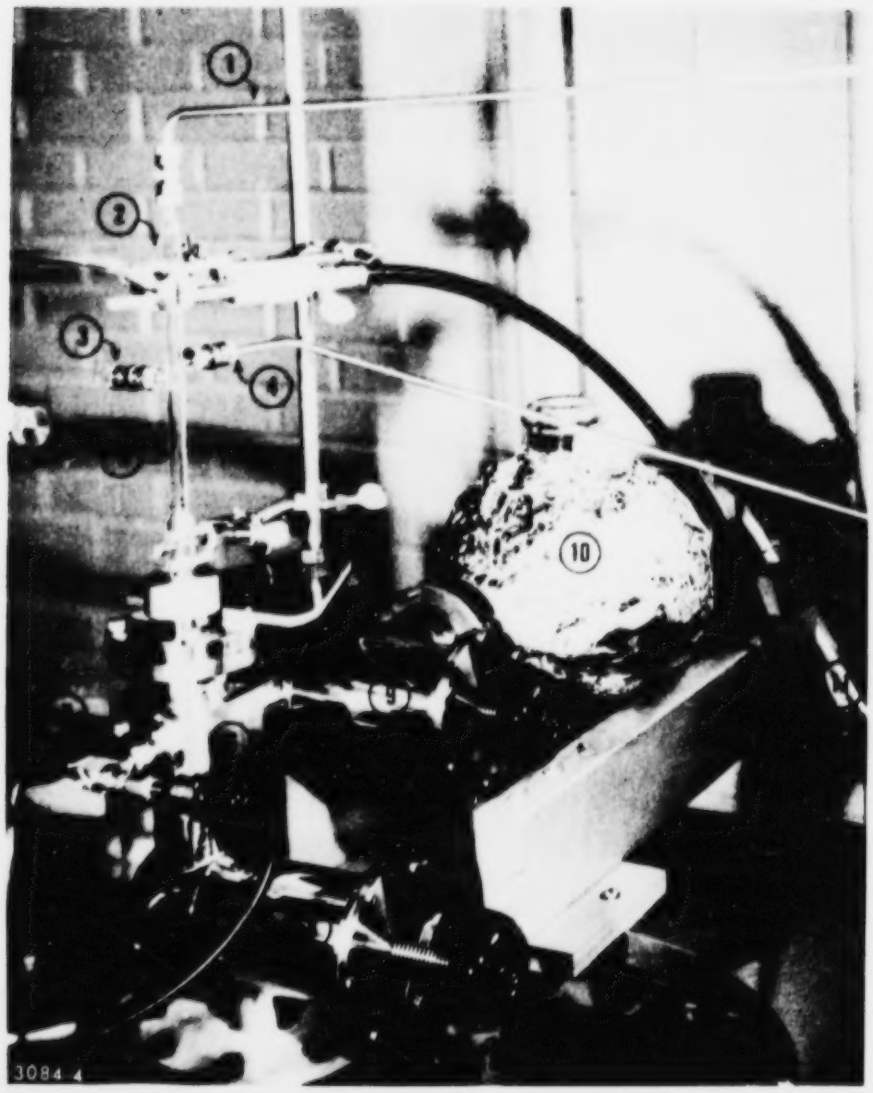


Figure 3. Detail of Reaction Chamber and Vacuum System.

(1) Oxygen Inlet Line
(2) Evenson Quarter-Wave Microwave Cavity
(3) Quartz Window
(4) Pollutant Gas Inlet
(5) Reaction Chamber
(6) Stainless Steel Vacuum "Cross"
(7) Vacuum Gauge Selector Valve
(8) 2" Vacuum Valves
(9) 2" Vacuum Valves
(10) Cold Trap
(11) Vacuum Line to Roughing Pump

geometry or function, was detachably mounted on one flange of a stainless steel "cross". A two-inch stainless steel bellows-type vacuum valve was affixed to the opposite side of the "cross" and was connected by flange to the high vacuum inlet of a Veeco high-vacuum pumping station. A similar vacuum valve was welded to the "cross" at a right angle to the reaction chamber. The outlet side of this valve was connected via a Delmar-Urry joint to a large cold trap and thence to a 450-liter/minute Welch Duoseal pump. A three-way valve flange-mounted to the remaining port of the "cross" provided a convenient point for measuring system pressure when experimental runs were in progress. Two pressure gauges covering a range of pressures from approximately one micron to 800 torr were connected to the system through this valve. Either gauge could be brought into the system at will. Because of the large size and weight of the vacuum system and because the 1.5-meter spectrograph could not be moved, the vacuum system was suitably positioned with respect to the spectrograph in order that the reaction chamber could be aligned with the spectrographic slit. The image of the chemiluminescent glow was then focused onto the slit by an appropriate spherical lens and the spectra of the glow were photographically recorded. Photoelectric measurements on glows in other reaction chamber designs could be similarly achieved without the necessity of moving or altering the vacuum system.

By closing the vacuum valve between the "cross" and the Welch Duoseal pump, the reaction chamber, gas lines, and regulators could be pumped down by the Veeco pumping station to a pressure of approximately 10^{-7} torr and effectively out-gassed with the aid of a heat gun. At this point, the reaction chamber was isolated by closing the valve between the chamber and the Veeco pump. Oxygen was admitted to the chamber until the pressure rose to approximately 20-30 torr while the Welch Duoseal pump was allowed to pump against the valve isolating it from the reaction chamber. This valve was opened slowly and the oxygen flow adjusted to give the desired flow rate. The gas was vented through the pump and discharged outside the laboratory. System pressure was adjusted by the gas flow and/or by throttling the pump.

5.3.3 Reaction Chamber

As was stated previously, preliminary optimization studies were performed to adequately define operating conditions leading to effective utilization of chemiluminescent glows in multi-air pollutant detection and assessment. Geometrical consideration of the reaction chamber and of the effect geometry has on the radiant efficiency and overall sensitivity of the system was of major practical importance. A variety of simple glass reaction chambers,

representing a fairly broad spectrum of configurations, were fabricated and evaluated in considerable detail. One configuration has already been shown (Figures 2 and 3). This and similar designs incorporating concentric flow tubes (Figure 4) were generally found to be undesirable for a variety of reasons. Two reaction chamber designs did emerge, however, that would satisfactorily meet the spectral and photometric requirements of the program.

The schematic diagram of the laboratory facility (Figure 1) depicts a spherical reaction chamber employed in the photoelectric detection scheme. This configuration worked very well in our studies, but does not necessarily comprise the most optimum reactor design since only limited time was available for geometrical considerations. A photograph of the spherical reaction chamber is shown in Figure 5. This reactor was fabricated from a one-liter Pyrex flask. A 25-mm I.D. Delmar-Urry O-ring joint was sealed to the flask and a quartz window was clamped onto this joint, to serve as an observation port. The O-ring provided a vacuum-tight seal. The gas inlets were 6-mm Pyrex tubes placed 120° from each other. The oxygen inlet tube was bent a short distance from its juncture with the flask in an effort to minimize the amount of radiation emanating from the microwave discharge zone that entered the reaction chamber. A short piece of cobalt glass tubing was employed at the terminal end of the tube to further reduce the level of extraneous radiation. An Evenson quarter-wave microwave cavity surrounded the oxygen inlet tube just above the bend. It served in producing oxygen atoms required for the chemiluminescent reactions. Pollutant gas was introduced through the opposite inlet into the chamber. Stainless steel gas lines were used throughout the system and were connected to the reaction chamber by means of two Cajon ultratorr vacuum connectors. The reaction chamber proper was connected to the stainless steel "cross" of the vacuum system by means of a simple "screw-on" O-ring connection.

Since the spherical reaction chamber was used entirely for the photometric phase of the program, it was mounted in a light-tight enclosure to ensure optical isolation. The light emanating from the chamber was directed through an optical filter and chopper onto a photomultiplier detector. Initially, the entire reactor was carefully covered with aluminum foil in an effort to collect all radiation possible. It was found that partial and selective covering of the chamber was more desirable because less background from the discharge zone was observed. Silvering a small area on the sphere immediately behind the quartz window seemed to produce the optimum effect.

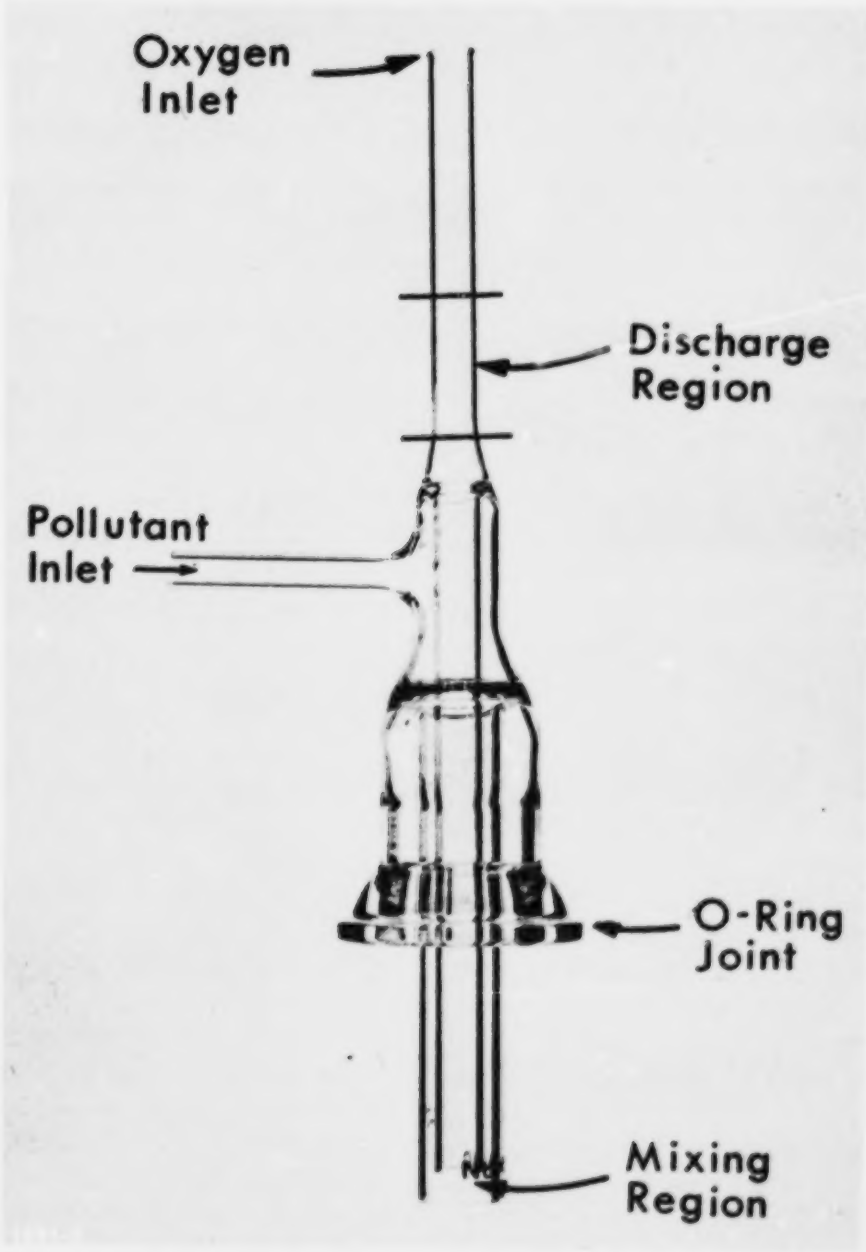


Figure 4. Concentric Flow Tube Reactor.

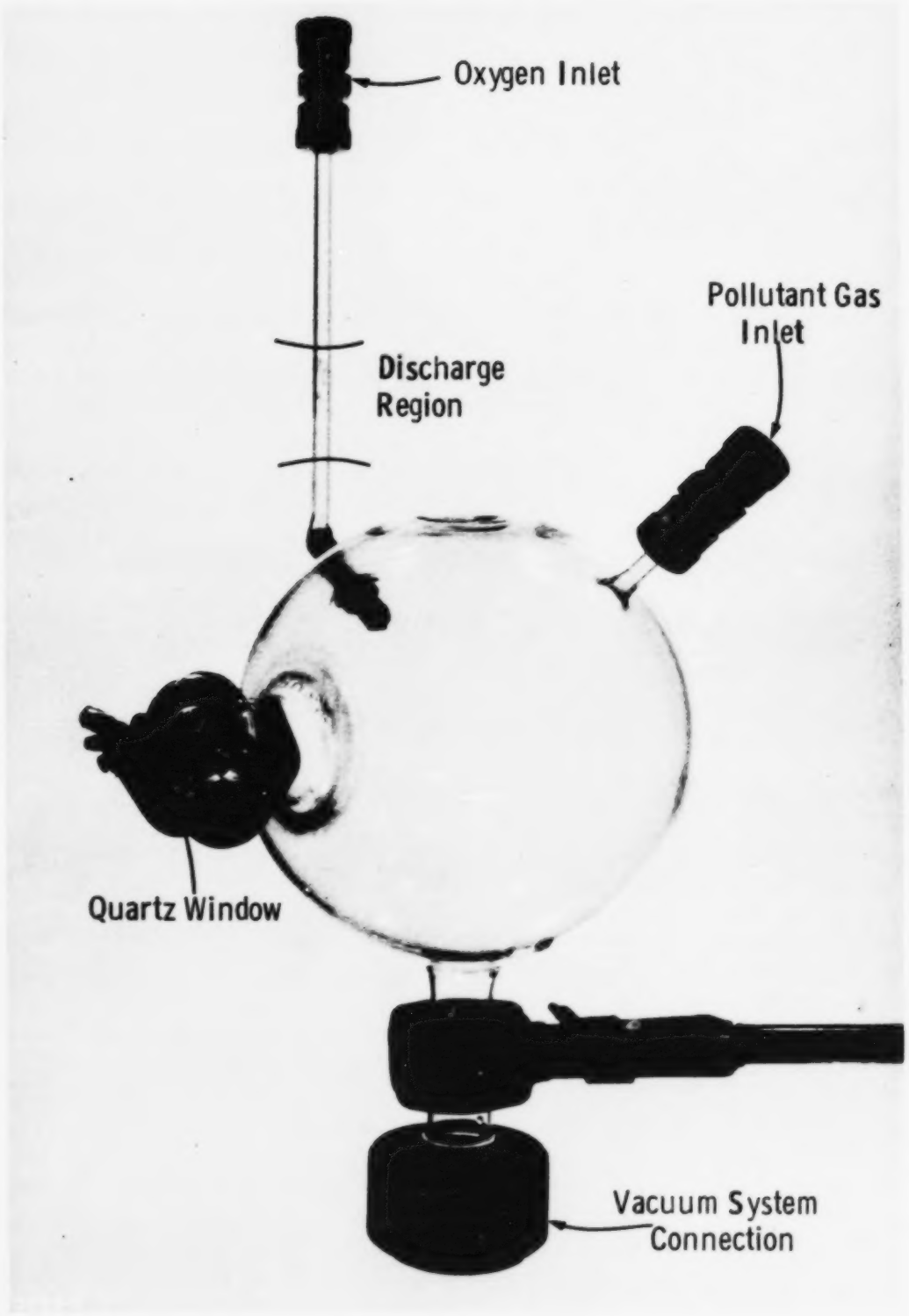


Figure 5. Spherical Reaction Chamber.

Fairly intense chemiluminescent glows were required for the spectral characterization phase of the program to enable photographing discernible spectra during reasonably short exposure times. The spherical reaction chamber was not well suited for this purpose and another reactor design was therefore required. A reaction chamber that did provide sufficient brightness is shown in Figure 6. The main body of this reactor was made from a 10-mm Pyrex tube. One end of this tube was bent at a 90° angle and reduced to a diameter of 6 mm. The 6 mm tube served as the oxygen inlet to the chamber and, as was the case with the spherical reactor, was surrounded by the microwave cavity. The pollutant gas inlet was another 6 mm tube sealed into the system just below the juncture of the oxygen inlet and the 10 mm tube. Cajon ultra-torr vacuum connectors were used as before for coupling the reactor with the gas handling system. The quartz window arrangement utilizing a Delmar-Urry joint was again employed as was the means for connecting the reactor to the vacuum system. This reactor provided an effective length of approximately 20 inches as viewed end-on. The 90° bend in the tube served to isolate as much as possible the radiation from the main discharge. This arrangement was aligned with the slit of the 1.5-meter spectrograph in a manner similar to that depicted in Figure 2. No optical isolation was required in this case but room lighting was extinguished when runs were being made. Addition of neat pollutant gases at a rate less than 5 cc/minute gave more than adequate exposures in a matter of a few seconds.

Some attempts were made to use this reactor configuration for photoelectric measurements. Spectral scans of a number of chemiluminescent glows were made with a 0.5-meter scanning monochromator fitted with a photomultiplier detector. The reaction chamber was not viewed end-on in this case but rather at 90° to its axis. Erratic results were obtained, which were attributable to a standing wave phenomenon visibly observable when high microwave power inputs were used. Bright bands moved up and down the tube causing anomolous "spectral" features to appear or vanish with respect to time. Some further design of this type of reaction chamber from a more fundamental fluid mechanical concept could, however, result in a highly efficient and sensitive system.

5.3.4 Oxygen Atom Generator

Although a variety of different methods are available for producing atomic oxygen and other atomic species, microwave discharge has been more widely used in recent years as an atom source. Fehsenfeld et al. (Ref. 28) attribute this popularity to a number of attractive characteristics which include: (1) simpler construction of sources; (2) no electrode contamination; (3) high degree of ionization (efficiency in producing O·),

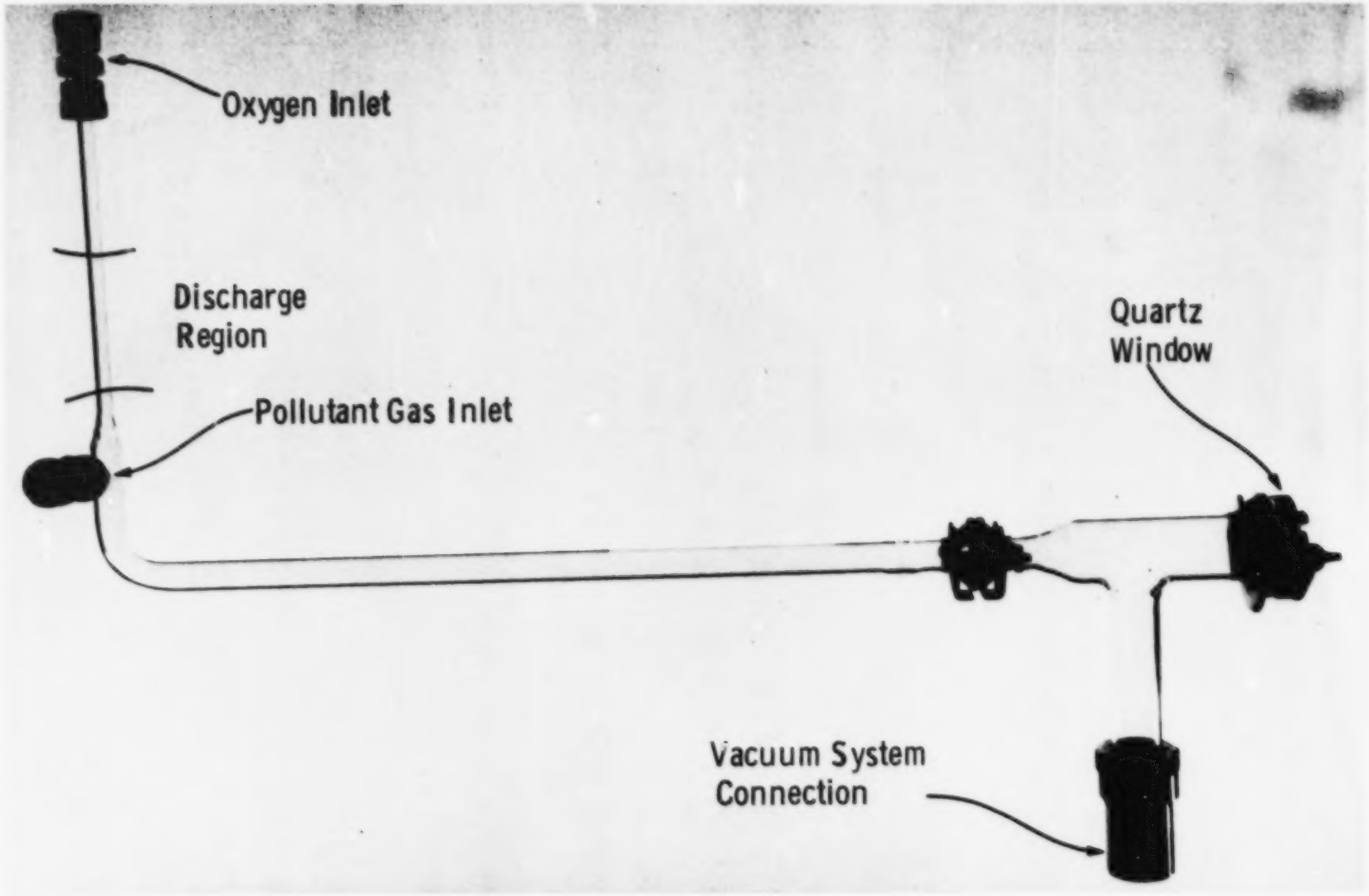


Figure 6. Tubular Reaction Chamber

and (4) elimination of dangerous high voltages. The choice of the microwave approach for this study, ir addition to the attributes just listed, hinged heavily on the fact that such equipment was available in the laboratory and considerable experience in generating microwave discharges for a number of different applications was at hand. Other means which would be less involved and more compact would obviously be considered when an instrument design based on the chemiluminescent approach is contemplated.

A Raytheon Model PGM-10X1 microwave generator delivering approximately 100 watts at an operating frequency of 2450 MHz was used as the power source in these studies. Ripple in this unit is reduced to one percent by filtering methods. Transmitted and reflected power determinations were made with a bi-directional meter which aided in tuning the resonant cavity. Two different cavities, a slotted waveguide and an Evenson quarter-wave cavity, were considered. The slotted waveguide represents one of the earliest microwave excitation sources and provides the useful feature that the cavity may be placed in position and removed without disassembling the system. It is unduly large and bulky, however, and was not very adaptable to our system. Operating efficiency was somewhat marginal as evidenced by large amounts of power reflected due to inadequate tuning adjustments. Of the several commercially available cavities, the Evenson cavity was found to be suited for the laboratory facility. The Raytheon generator cable coupling is readily adaptable to the cavity fitting and the geometry of the cavity is ideally compatible with the reaction chamber designs (Figure 3). The Evenson cavity has both tuning and coupling adjustments, which is an appropriate feature for discharge application. When properly adjusted, the cavity can maintain discharges at pressures ranging from less than one micron to over 700 torr while reflecting less than one percent power. Air cooling must be provided when the cavity is under power.

Some difficulty was experienced in our initial photometric measurements that could be traced to the Evenson cavity. Large fluctuations were observed in the discharge which were reflected in erratic background. Vibration of the cavity was found to be the problem and was corrected. Movement of the cavity with respect to the discharge tube results in a somewhat drastic change in loading characteristics and hence power input to the gas. More rigid mounting and vibrational isolation was the obvious solution.

5.3.5 Detection System

In view of the dual nature of this program, two distinct detection modes were required for data acquisition. Spectral characterization of the chemiluminescent glows resulting from the reaction of NO, CO, and SO_2 with atomic oxygen was accomplished by photographically recording the emission spectra in the ultraviolet to the near infrared region. Figure 2 gives a typical representation of the experimental set-up employed for this phase of the study. The reaction chamber shown in this figure was replaced, however, with the one depicted in Figure 6 and discussed in Section 5.3.3. The reaction chamber was aligned with respect to the spectrographic slit and the image of the glow focused onto the slit by a spherical lens. A Jarrell-Ash 1.5-meter plane grating spectrograph was used in taking spectra. This instrument gives a linear dispersion of 11 A/mm and has adequate speed to ensure recording bright spectra from fairly weak sources in reasonable exposure times. The spectra are recorded on 4 x 10 in. spectrographic plates with emulsions appropriate to the wavelength region of interest. A Jarrell-Ash Model 24-300 precision recording microphotometer was used in the reduction of the spectrographic data. The instrument locates photographically recorded spectral lines with a precision of plus or minus 5 microns over a 25-millimeter range, measuring line density over a range of 0 to 3.5 or better.

Photometric measurement of the radiant intensity resulting from the chemiluminescent reactions comprised the largest fraction of the experimental program. A schematic diagram of the facility employed in making these measurements was shown in Figure 1. The spherical reactor was used for all photometric measurements and was enclosed in a light-tight box with elements of the detection system which included

(1) An optical filter consisting of either a Schott type IL-674, IL-456, or UV-IL-351 depending on the chemiluminescent glow under study,

(2) An electro-mechanical chopper,

(3) An EMI 9558 QB photomultiplier detector and power supply,

(4) A Brower Model 131 "Lock-In" amplifier, and

(5) A Honeywell AZAR recorder.

In this detection mode, the radiant output of the spherical reaction chamber was modulated by an electromechanical chopper blade positioned in line with the highly sensitive photomultiplier

detector. The optical filter placed in the beam limited the bandwidth of the luminous signal impinging on the detector. Since the overall signal to noise ratio (S/N) of any detector/amplifier system is proportional to the system bandwidth, the bandwidth must be limited to the lowest possible usable value, but must not be so narrow as to make the observation time excessive. Usually a trade-off must be made.

The photomultiplier detector is essentially a constant current device and the choice of the proper load resistor associated with it must be made with care. It should be as high as possible in resistive value but not so high as to have the shunt capacitive effects alter the chopped waveform from a near perfect square-wave. In the system employed, the output of the photomultiplier tube was fed to an AC carrier-type amplifier. This amplifier was of the special design known as a "lock-in" amplifier. An AC amplifier was used to offset any DC drifts, which degrade the signal-to-noise ratio of the system. The amplifier was a high gain, narrow bandpass type, which was tuned to amplify only at the chopping frequency set by the electro-mechanical chopper. To recover the output signal in its original DC form, a synchronous detector was employed. This detector received the chopped/amplified signal from the photomultiplier and that signal was compared to a reference carrier developed to be in a known phase relationship to the original chopper position. The phase relationship was due to electromechanical system lags. Output from the detector was fed to the Honeywell recorder to obtain a graphical record.

The high voltage supply for the photomultiplier tube was an adjustable output, regulated type. Adjustable output allowed photomultiplier gain adjustment and sensitivity equalization, while the regulation reduced gain variations to an absolute minimum.

Another valuable circuit was the auto-zero control. This circuit in the system balanced out background variations due to dark current variations, and variance in the background luminescence resulting from nitrogen oxide impurities in the atomic oxygen stream. Its action was controlled by the system programmer.

While this system may sound overly sophisticated for our study, the many advantages it offers in contrast to DC amplification approaches make it highly desirable for photometric applications encountered in our experimental work. Other amplifiers, obviously, could be (and have on occasion been) employed. While little was known about the equivalent signal output of one ppb NO, CO, or SO_2 at the onset of this program, a detection system exhibiting a wide range of gain and promoting maximum signal-to-noise ratio would be the logical choice. In the

development of a field monitoring instrument, a more fundamental appraisal of electronic requirements would be made with respect to that particular and specialized application.

5.3.6 Gas Flow Metering and Mixing System

A gas flow metering and mixing system was required to meter and deliver known and variable oxygen and/or oxygen-argon mixtures as well as pollutant gas flows to the reaction chamber. Such a system was designed and fabricated for use in this program and is shown schematically in Figure 7. Basically, this system comprised two distinct parts, which will be discussed separately.

One part of the flow system controlled the oxygen flow to the reaction chamber and consequently was intimately associated with the level of atomic oxygen produced. Known mixtures of oxygen and argon could also be made and delivered at predetermined rates to the reactor. These mixtures were studied in a limited way in order to see to what level the background radiation (due to nitrogen impurities in the oxygen) could be reduced. Both the oxygen and argon flows were controlled by critical orifices placed in the gas lines. One test gauge served for measuring the upstream pressure in each case. The calibration of the critical orifices in terms of flow rate as a function of upstream pressure was accomplished with a Brooks Instrument Company "VOL-U-METER". Flow calibration was checked periodically during the course of experimental measurements. The entire system was vacuum tight and could be pumped down to pressures approximating 10^{-7} torr.

The second part of the flow system delivered known concentrations of NO, CO, and SO_2 to the reaction chamber. Diluent gas (air, nitrogen, argon, etc.) was metered through a critical orifice. A test gauge was employed to measure upstream pressure and flow calibration of the orifice established in terms of this pressure as before. Pollutant gases and/or pollutant gas mixtures were added to the diluent stream downstream of the critical orifice in that line. By varying the addition of pollutant gas to the diluent stream, varying concentrations of the pollutant could be delivered to the reaction chamber.

Two alternatives were available for metering known quantities of the pollutant gas into the diluent stream; these differed only in the flow range covered. When pollutant gas mixtures such as 10 ppm NO in argon, for example, were employed, known gas additions to the diluent stream were made using a Hasting-Raydist mass flow meter covering flow ranges of 0-0.5 cc/min and 0-5 cc/min. Flow regulation was achieved by a fine metering valve placed between the mass flow meter and the diluent gas line.

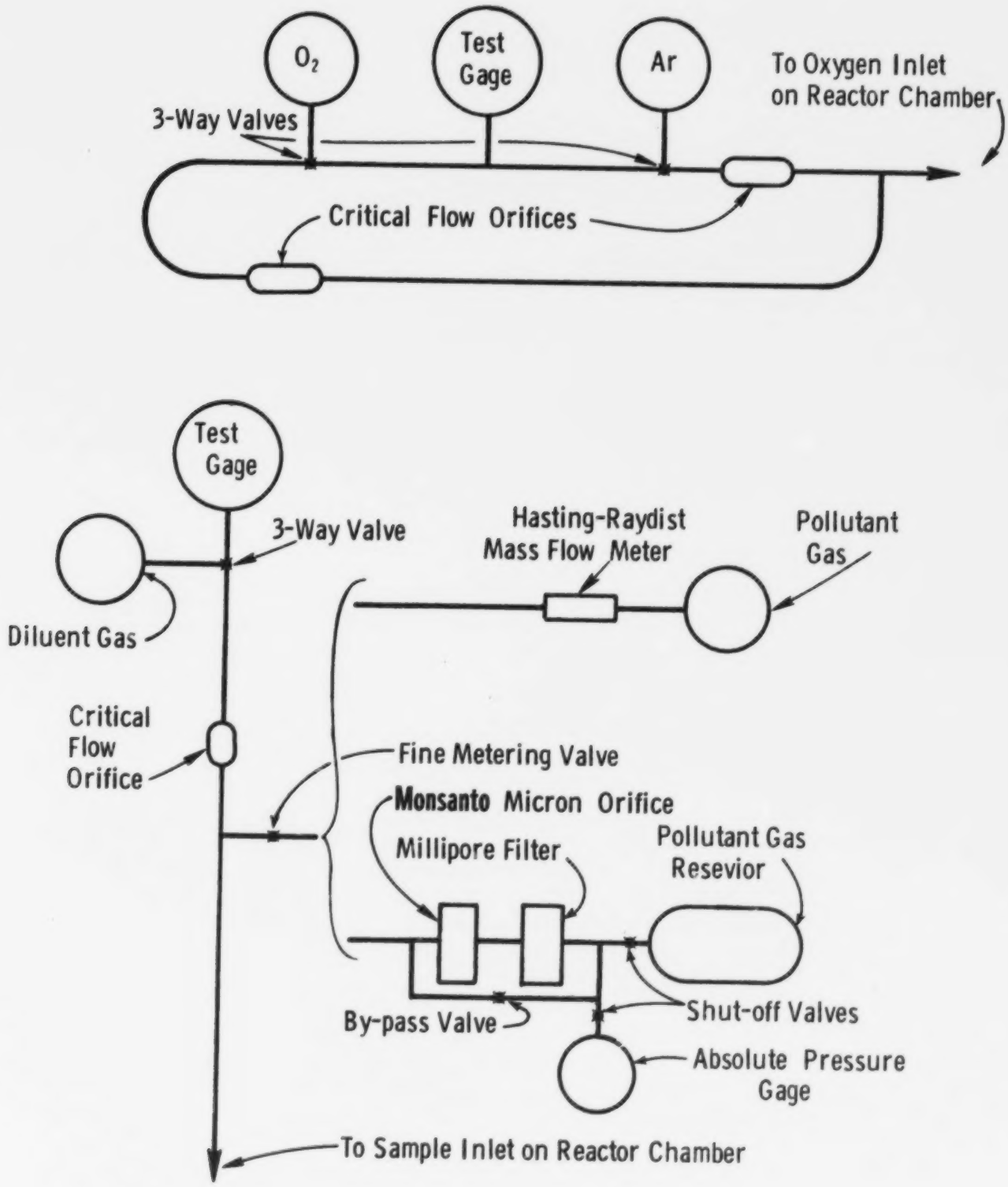


Figure 7. Schematic of the Gas Handling System.

Undiluted pollutant gases could be added to the diluent stream in sufficiently small quantities to result in pollutant concentrations in the low ppb range. In this case, a quartz Micron-Orifice manufactured by Monsanto Research Corporation was employed as the flow control device. Pollutant flows as low as 10^{-6} cc/min can be achieved with this type of orifice. Change in flow through the orifice was controlled by the upstream pressure.

The entire flow system was constructed from materials compatible with the various gases used in this study. An overall view of the system showing its relative compactness is shown in Figure 8. Gas lines leading from this system to the two inlets of the reaction chamber were of stainless steel.

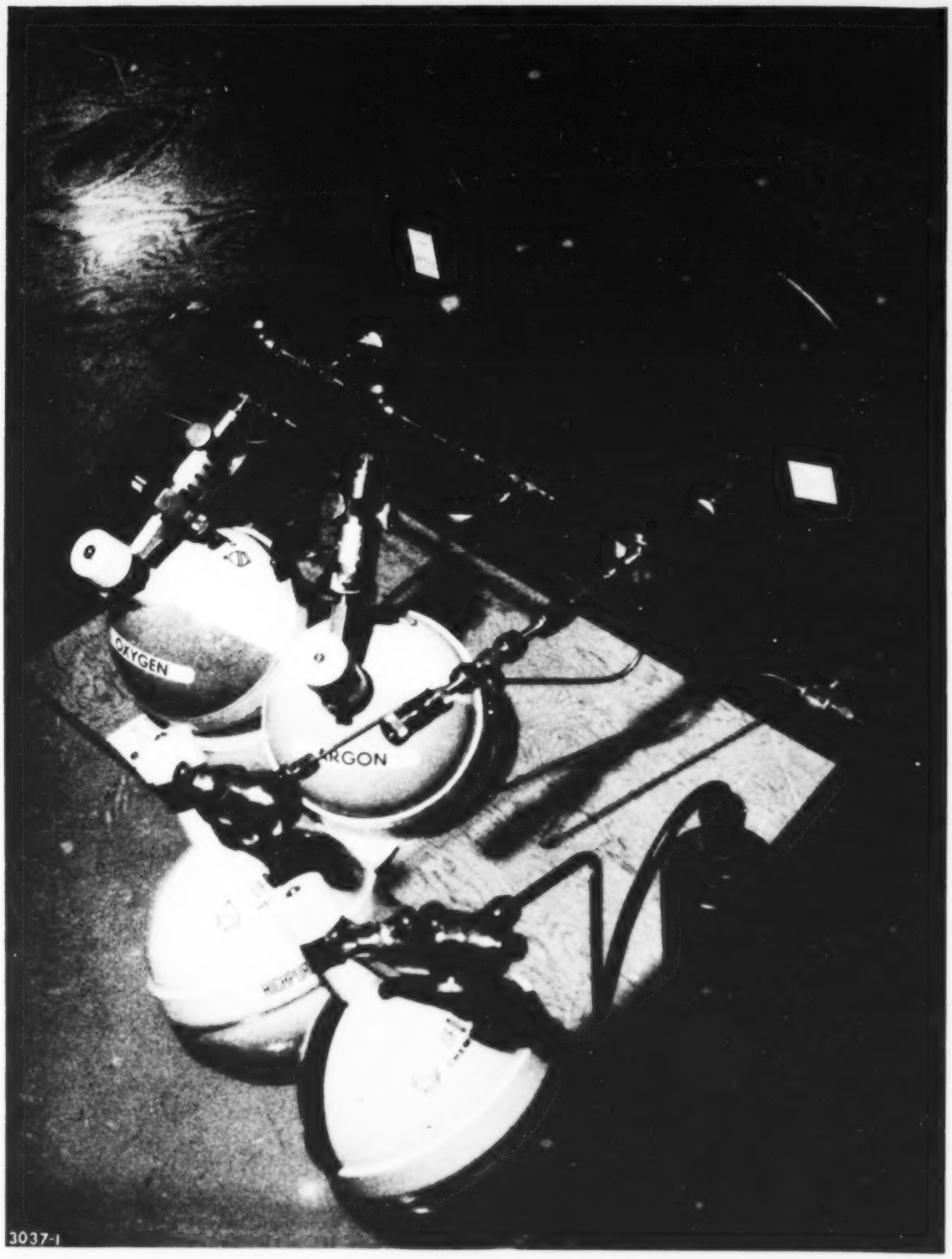


Figure 8. Overall View of the Gas Handling System.

6. EXPERIMENTAL RESULTS

6.1 SPECTRAL DISTRIBUTIONS OF THE CHEMILUMINESCENT GLOWS

As discussed in Section 4, the spectral distributions of the chemiluminescent glows resulting from the reaction of NO, CO, and SO_2 with atomic oxygen have been determined by others previous to this study. However, the conditions of the reaction, the source of energy to produce atomic oxygen, and concentrations of the gases vary widely from study to study. It was necessary therefore to confirm the earlier results employing the 0-100 watt microwave discharge system.

The characterization effort was conducted employing the cylindrical reactor shown in Figure 6. In general, the reactor total pressure was maintained near one torr, the Raytheon generator was operated at 50% of power and the oxygen flow was set at 330 cc/min. A low flow of the pure pollutant gas (generally less than 5 cc/min.) was introduced into the reactor and the cylinder was viewed end-on in order to maximize intensity for short exposure times.

The spectral distributions were determined both photographically employing the 1.5-meter Fastie Jarrell-Ash spectrograph (Figure 2) and by photomultiplier detection using the 0.5-meter Jarrell-Ash scanning monochrometer. Figures 9 through 11 present the spectra and the densitometer traces of the chemiluminescent glows.

The spectral distributions observed in the cases of NO and CO agree exactly with earlier published work. The spectral distribution from the SO_2-O reaction, however, indicated continuous emission over the region from approximately 3000 A to 4100 A with a maximum emission at 3500 A. Halstead and Thrush (Ref. 27) have summarized the intensity distribution from the SO_2 afterglow and have identified three distinct emission modes, which they term the α, 1, and 3 systems. Figure 12 presents the relative intensities of these three systems.

The spectral distribution obtained by the microwave discharge approach, where the SO_2 gas is admitted to the reactor downstream of the discharge, apparently results in chemiluminescent emission characteristic primarily of system 1, and does not include α or 3 emission. The α emission, which is most intense, is observed when the SO_2 is discharged by RF energy at about 300 watts. When the SO_2 was passed with oxygen through the Evensen cavity, no change in the spectral distribution was observed from that illustrated in Figure 11. Since the theoretical sensitivity of the

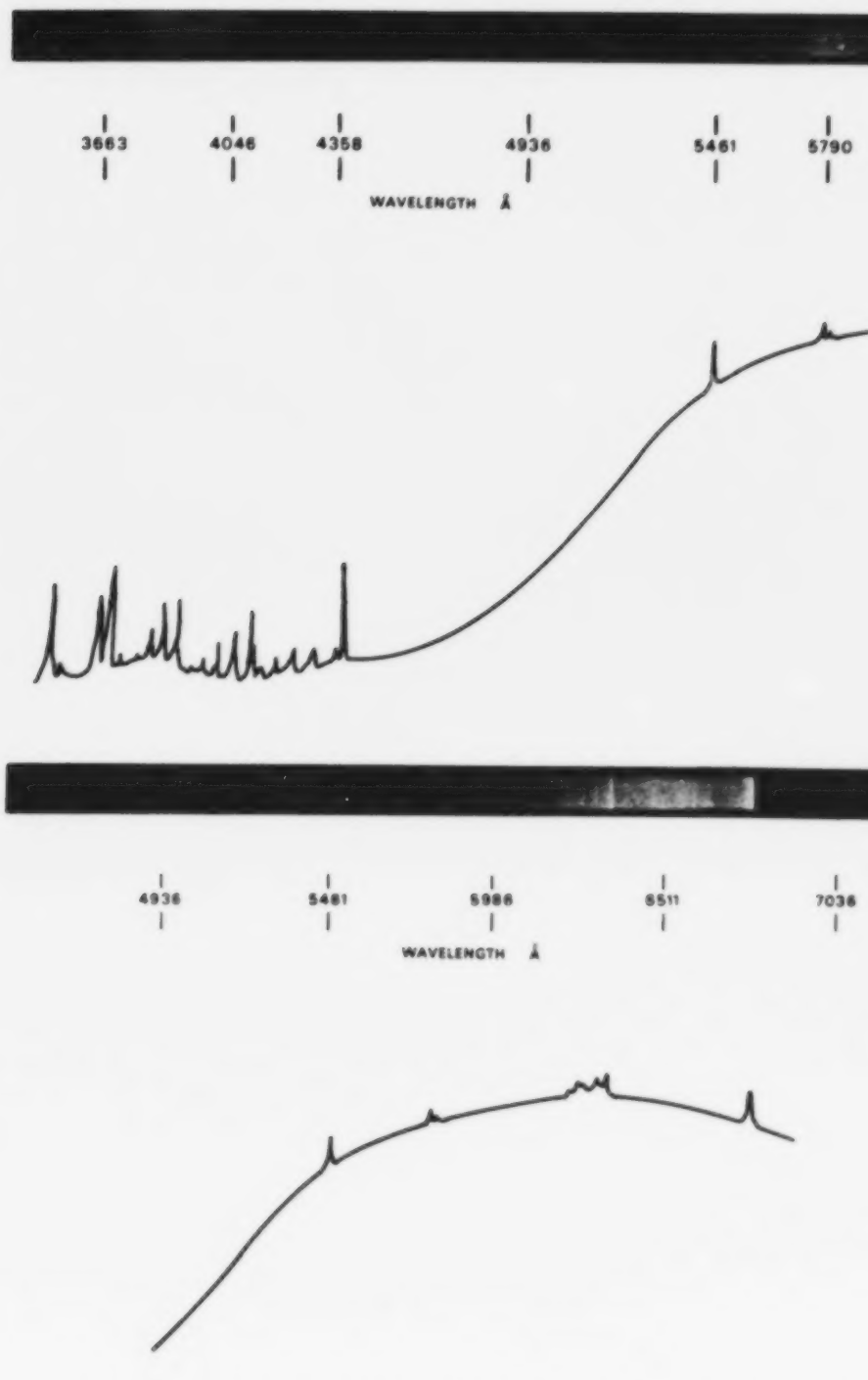


Figure 9. Spectral Distribution of the NO-O Chemiluminescent Reaction.

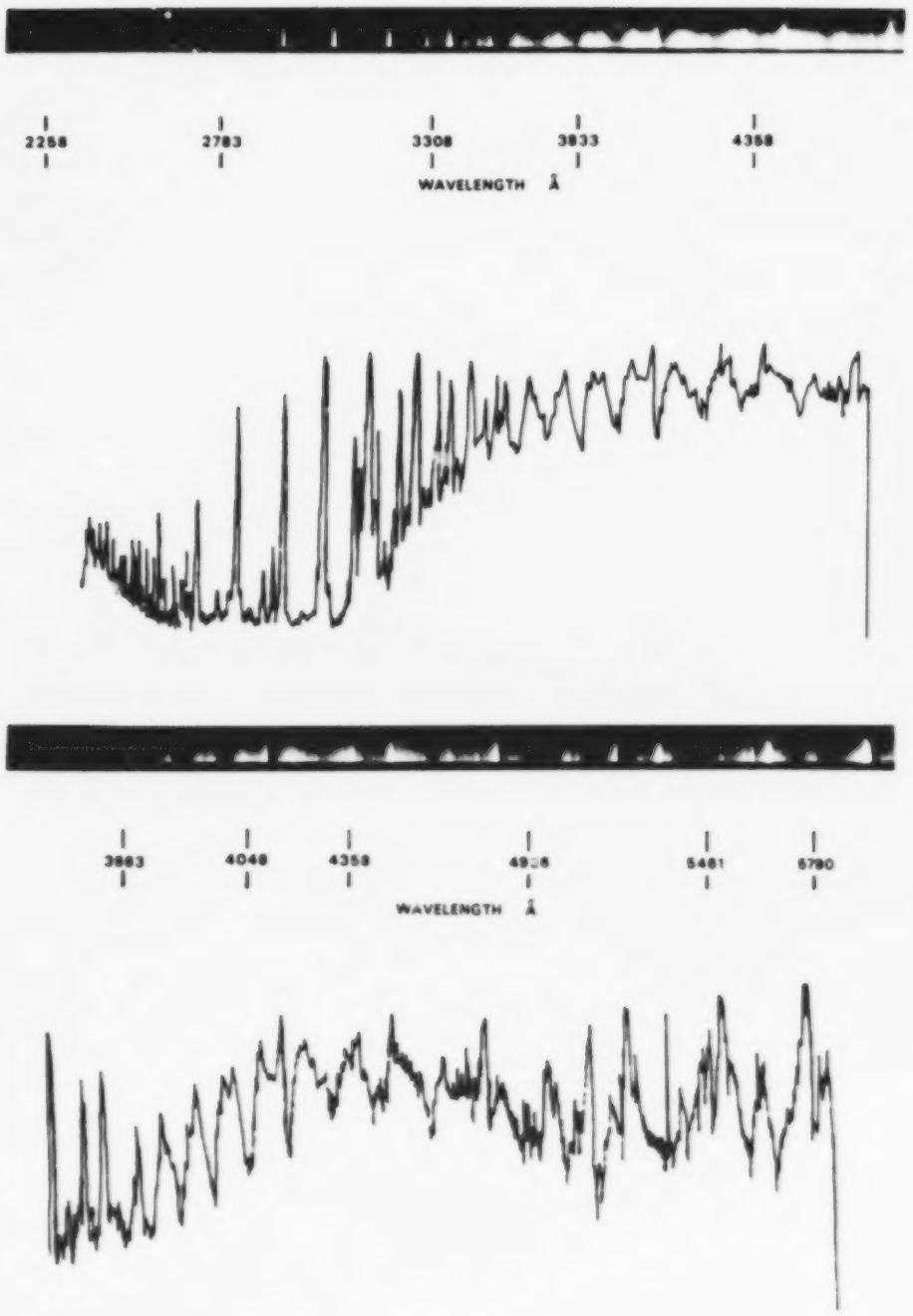


Figure 10. Spectral Distribution of the CO-O Chemiluminescent Reaction.

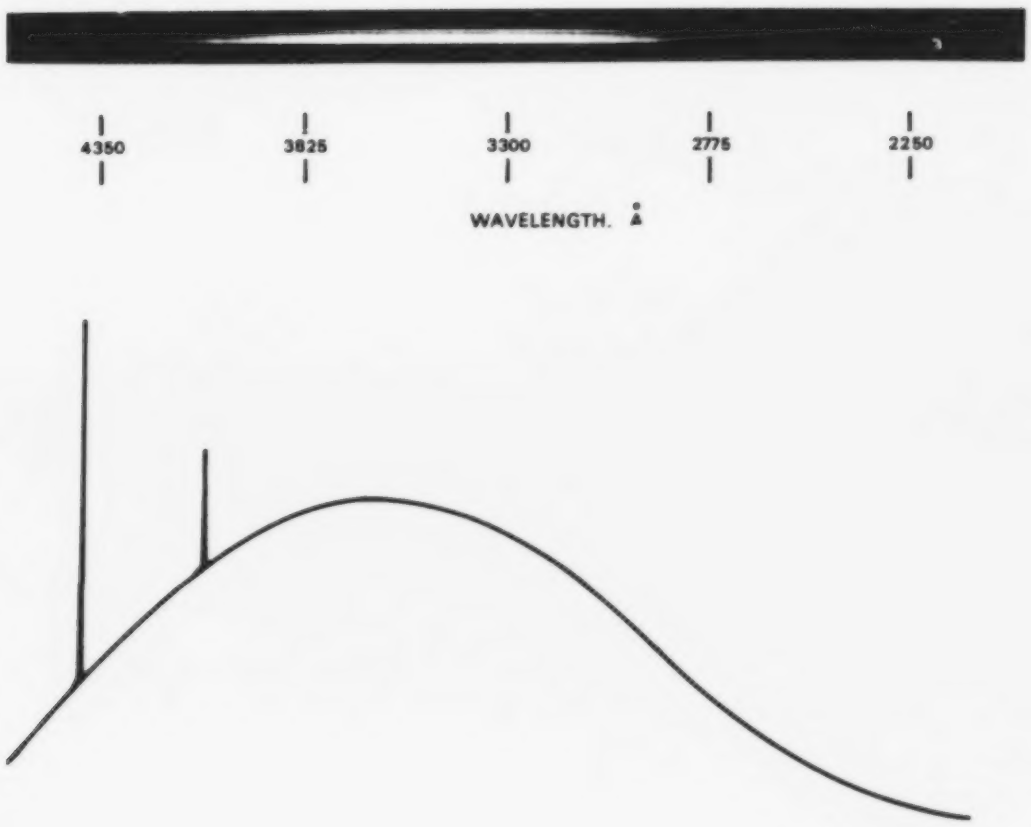


Figure 11. Spectral Distribution of the SO_2-O Chemiluminescent Reaction.

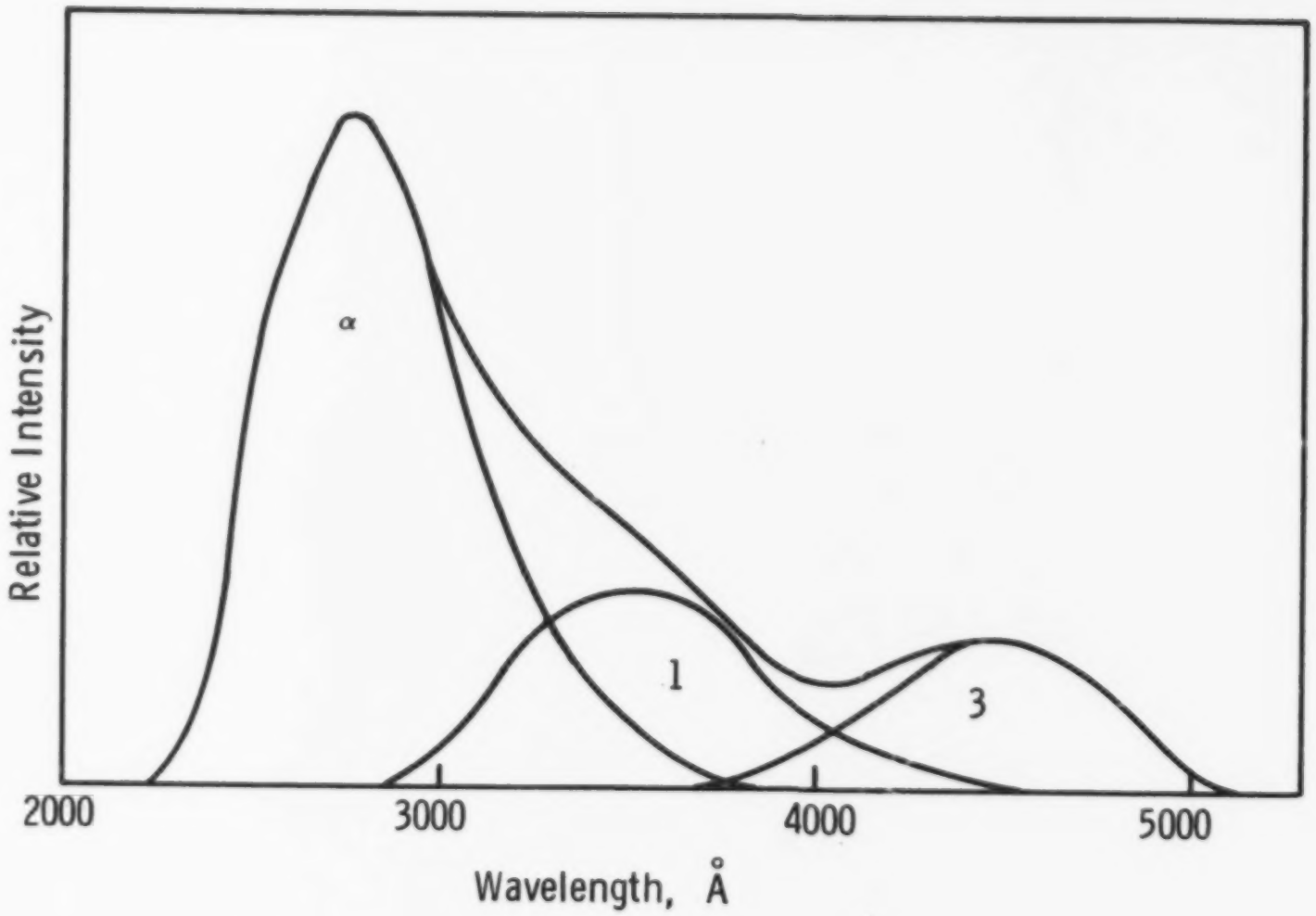


Figure 12. Intensity Distribution of the Sulfur Dioxide Afterglow.

SO_2-O reaction is orders of magnitude higher than that required to detect SO_2 at 1 part/billion concentration, the absence of the intense α system in the chemiluminescent emission does not necessarily jeopardize the feasibility of this approach.

Based upon the distributions observed it is apparent that the use or narrow band-pass filters will permit the isolation of spectral regions characteristic of each pollutant without interference from the other two components of interest. For the NO-O reaction, a filter that transmits in a wavelength region centered at 6500 A would be ideal. For CO-O, this peak transmission region should be a 4350 A, and for SO_2-O, the filter should transmit in a wavelength region centered at 3500 A.

From the spectra it can be concluded that some difficulty should be anticipated in detection of the relatively weak banded emission from the CO-O reaction. The continuous emissions characterized by the NO and SO_2 systems are much more amenable to photoelectric detection via interference filters.

6.2 SENSITIVITY AND CALIBRATION OF THE GLOW REACTIONS

6.2.1 General

The lower limits of detection of NO, CO, and SO_2 via chemiluminescent reactions with atomic oxygen and the calibration of intensity versus concentration of the pollutant gases were determined employing the one-liter spherical reactor shown earlier in Figure 5.

General guidelines stated for the detectable ranges desired for the various pollutants were given as follows:

Gas	Range
NO	1 ppb - 0.5 ppm
CO	0.5 ppm - 50 ppm
SO_2	1 ppb - 0.7 ppm

The conditions for these experiments normally included a total reactant pressure of 0.85 torr, 50% of power, an oxygen flow rate of 330 cc/min at STP and diluted pollutant flow rates between 0-5 cc/min. The detection system, which has been described in detail in Section 5.3.5, consisted of a mechanical chopper, an interference filter, the EMI 9558 photocell, Brower "Lock-in" voltmeter and a Honeywell AZAR recorder.

Preliminary to these studies, the effects of percent of microwave power and pressure on the intensity of the neutral oxygen atom lines produced after the O_2 discharge were determined. This study was undertaken to optimize the microwave discharge conditions for maximum dissociation. Both the Evenson cavity and a Raytheon slotted waveguide were studied. The Evenson cavity proved to be the most effective of the two in producing atomic oxygen, as would be expected from our earlier discussion in Section 5.3.4. Changing power to the discharge cavity had only a slight effect on the oxygen atom concentration above about 30% power output at the generator. This finding was in keeping with the results reported by Brown (Ref. 29) where a twofold increase in oxygen atom concentration was observed when the power level was raised from 4 watts to 20 watts, while no further increase occurred when the power was increased from 20 watts to 85 watts. From the spectral data taken, oxygen line intensity appeared to remain constant over an increase in reaction chamber pressure ranging from 0.18 to 0.50 torr. Decrease in oxygen atom concentration would be expected, however, if pressure was increased sufficiently to cause increased wall recombination effects and/or the amount of molecular oxygen dissociated.

6.2.2 The NO-O Chemiluminescent Glow

The lower detection limit study and calibration of the NO reaction intensities were carried out employing two NO gas mixtures as follows:

10 ppm NO in argon (Lif-O-Gen)
580 ppm NO in nitrogen (Matheson)

The NO concentrations in the mixtures were verified by mass spectrometric analysis before and after use. The stability of the mixtures was amply supported by the duplication of glow intensities under identical conditions from day to day.

Variable flow rates of these mixtures were admitted into the spherical reactor by use of Hastings-Raydist mass flowmeters with ranges of 0-5 cc/min and 0-0.5 cc/min flow. The mass flowmeters are normally calibrated in terms of air flow rate, but correction factors can readily be applied to convert these readings to flows based on argon or nitrogen. These conversion factors were tested by secondary flow calibration using a Brooks Vol-U-Meter.

Because of the ability of the lock-in voltmeter to retrieve a weak signal in the presence of background noise, no effort was made to prepurify the oxygen supply to the microwave cavity. While in some cases Lif-O-Gen high purity oxygen containing less than 5 ppm nitrogen was employed, the studies reported here were

conducted using Matheson tank oxygen, which has an average nitrogen concentration of about 15 ppm. In the microwave cavity, this nitrogen impurity is partially converted to nitrogen oxides, which react with atomic oxygen to yield chemiluminescent glow characteristic of the pollutant of interest. In most experiments this background glow was found to be equivalent to approximately 6 ppm of nitric oxide.

The concentration of nitric oxide presented in the calibration curves of Figures 13 and 14 were calculated by consideration of the extent of dilution of the pollutant in the spherical reactor assuming no dissociation of oxygen. That is, if the oxygen flow rate was set at 330 cc(STP)/min and the flow rate of a 10 ppm nitric oxide in argon mixture was 1 cc/min, the concentration of nitric oxide in the glow reactor would be:

$$NO_{ppb} = \left[\frac{V_{Mix}}{V_{O_2} + V_{Mix}}\right]\left[\frac{10}{10^6}\right] = \left[\frac{1(10)}{10^6(331)}\right] = 30.2 \text{ ppb}$$

Calibrations of the NO-O glow intensity was obtained by use of a Schott interference filter with a maximum transmission at 6740 A and a half-width of 125 A. In Figure 13, representative results of intensity versus concentration are presented when the 580 ppm NO in N_2 mixture was employed. In this case 100 percent intensity corresponds to a gain of 2.5×10^{-9} amperes. As expected, the intensity is found to be linear with concentration from seven ppm down to 200 ppb. The complete study showed that this linear relationship was maintained up to concentrations in excess of 3000 ppm.

In Figure 14, representative data recorded using the 10 ppm NO/argon mixture are presented. One hundred percent intensity for these measurements corresponds to a gain of 1×10^{-9} amperes. Again the response is linear with concentration from 70 ppb down to 6 ppb, which approaches the lower limit of detection employing this specific combination of equipment. In Table I the reproducibility of the calibration data is presented based upon a least-squares computer fit of results obtained over a period of two weeks using a regression analysis (Ref. 30).

For particular sets of data taken during a single run, the confidence limits for a least-squares linear relationship in all cases exceeds 99.5. The slopes calculated are in units of relative intensity/cc/min flow of the 580 ppm NO in N_2 mixture. The deviation of the slope of the intensity versus concentration curve for individual sets of data from an average value obtained by including all data was found to be less than 3% in the case of

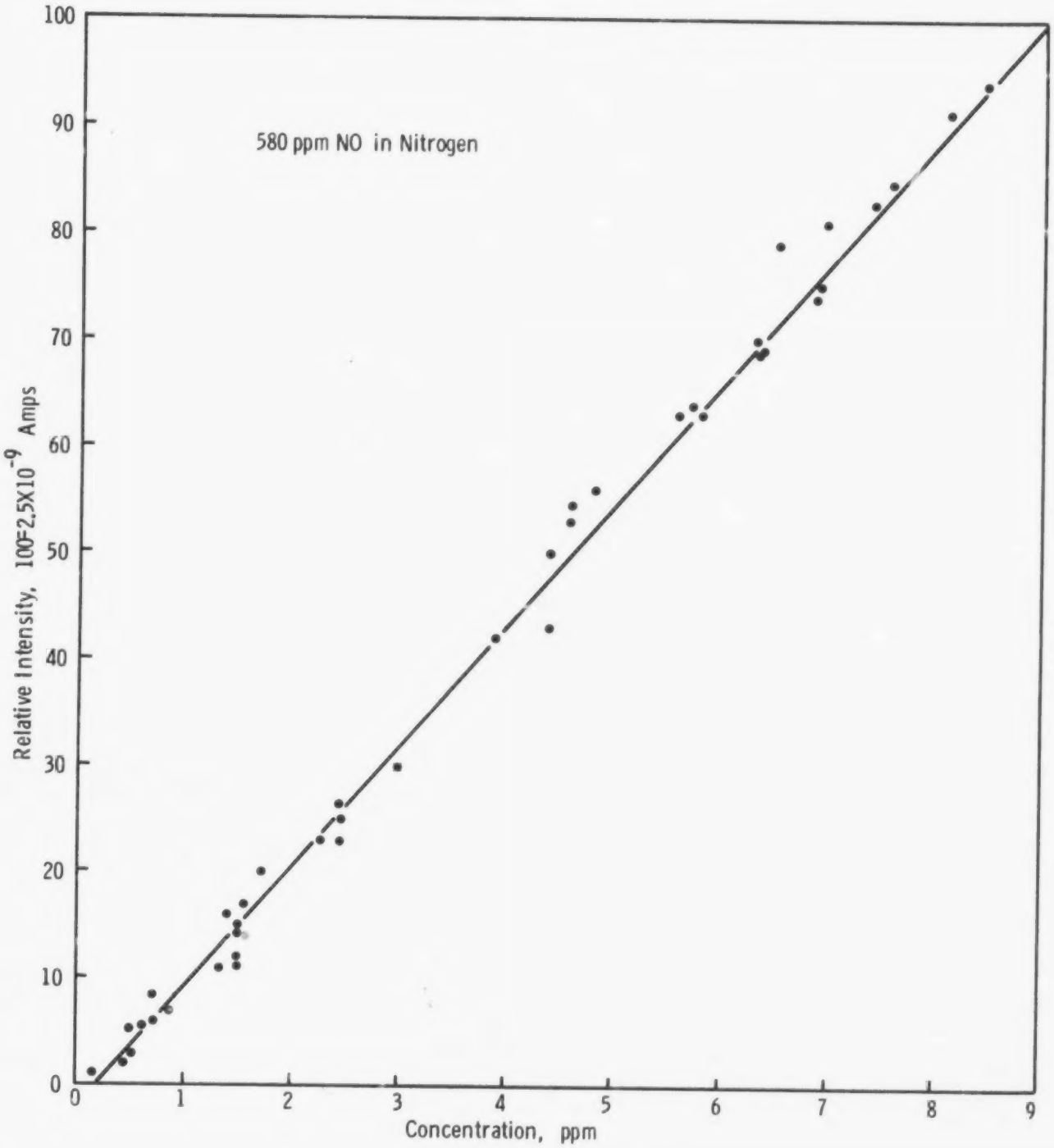


Figure 13. Calibration Curve for Nitric Oxide.

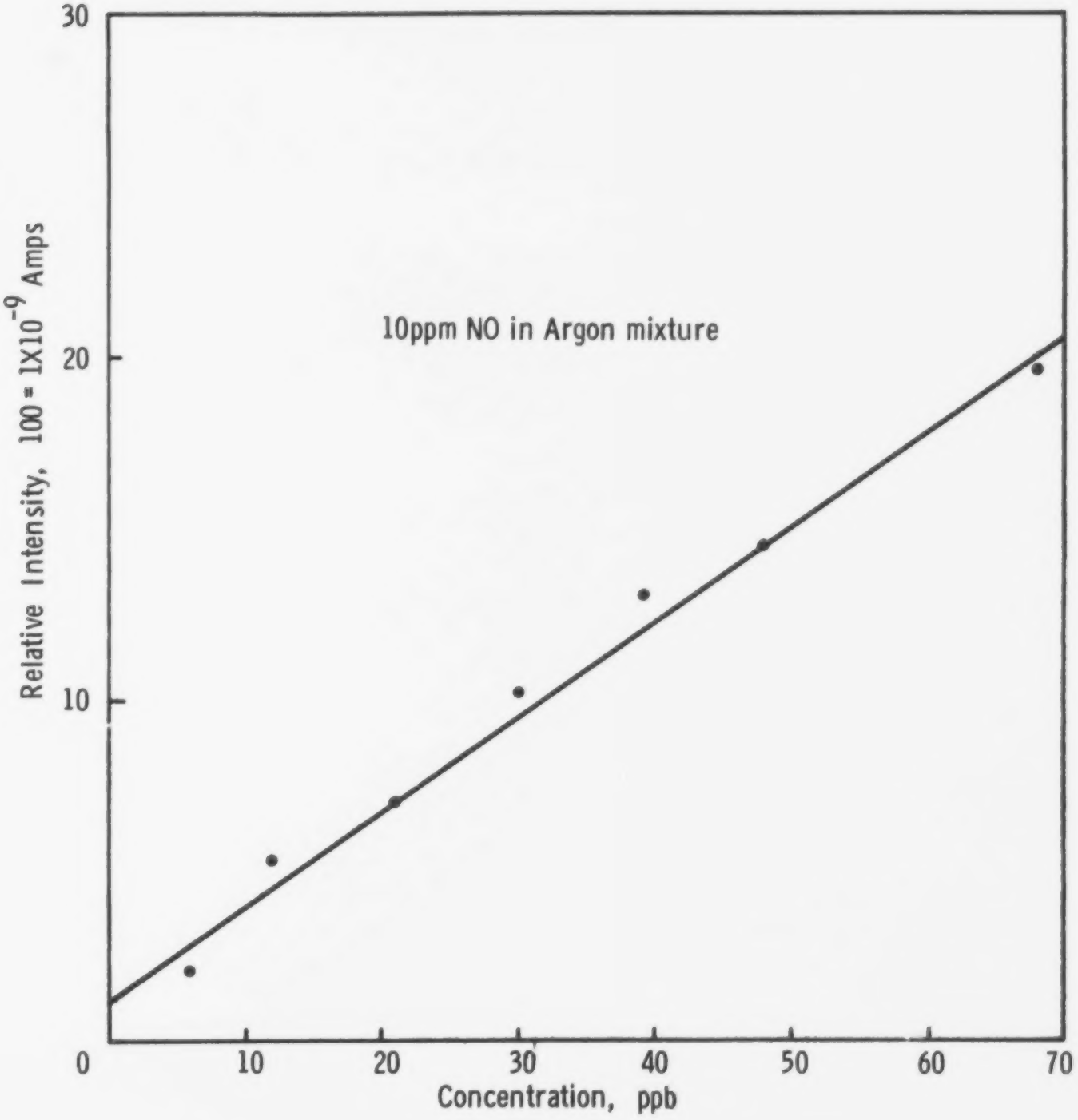


Figure 14. Calibration Curve for Nitric Oxide.

Table I

REPRODUCIBILITY OF THE NO-O REACTION

580 ppm NO/Nitrogen

Data Set*	Slope	Intercept	Confidence Limit
1	19.82	-1.67	99.96
2	20.39	-4.68	99.82
3	21.64	-1.96	99.92
4	20.50	-1.41	99.68
5	19.07	-2.47	99.60
6	19.98	-2.96	99.64
7	19.76	-0.66	99.89

Conditions: O_2 flow 330 cc/min, 50% of power, 0.85 torr.

*Data sets consist normally of from 5 to 10 separate points.

the 580 ppm NO/N_2 mixture. The slope of all data in nitrogen diluent was found to be 2.8 x 10^{-10} amperes/ppm NO. This value represents the behavior characteristic of 46 data points taken on separate days in seven sets.

The difference in slopes of the argon versus nitrogen diluent calibration curves is presumed to be associated with the efficiencies with which the diluent gas behaves as a third body in collisional deactivation of the excited NO_2 species by means of other than chemiluminescent emission. The slope of intensity versus concentration curve with argon diluent was approximately 10 times more sensitive than that with N_2 diluent and gave a value of 2.8 x 10^{-9} amperes/ppm NO.

Figure 15 demonstrates the effect of the percent of power employed in the microwave discharge on the emission intensity; 50, 60 and 70% of power yield substantially the same linear relationship. However, in this limited study, there appears to be a small trend to higher intensity at higher power since the three 70% points fall above the curve. Below 30% of power the intensity of the NO-O glow was observed to fall off rapidly due to the decrease in efficiency of the oxygen microwave discharge process.

Figure 16 demonstrates the rather strong influence of reaction pressure on the intensity of the NO-O glow reaction. In this case the sensitivity of the reaction is higher at 0.85 torr than that at 0.25 torr. These results suggest that total pressure must be rather closely controlled in the design of a monitor based on the chemiluminescent principle.

Very good instrumental response is demonstrated in the case of nitric oxide. As is illustrated in Figure 17, maximum deflection was attained in less than 18 seconds. Successive reduction in NO concentration into the reaction chamber is shown by the stepped decay curve and again illustrates the fast time response with which corresponding NO concentrations find their level. Much faster response times would, of course, be exhibited by an optimized instrument since one could dispense with much of the "plumbing" incorporated into the laboratory facility.

The practical lower limit of detection of the chemiluminescent glow is, of course, much lower than 6 ppb. The use of a blocking filter that would not transmit radiation below 6500 A but would pass wavelengths up into the infrared region would greatly enhance the sensitivity of the detecting system. Further increases in sensitivity would be realized by optimization of the reactor geometry to ensure that a much higher proportion of the emitted light reaches the detector. The fact that the practical lower

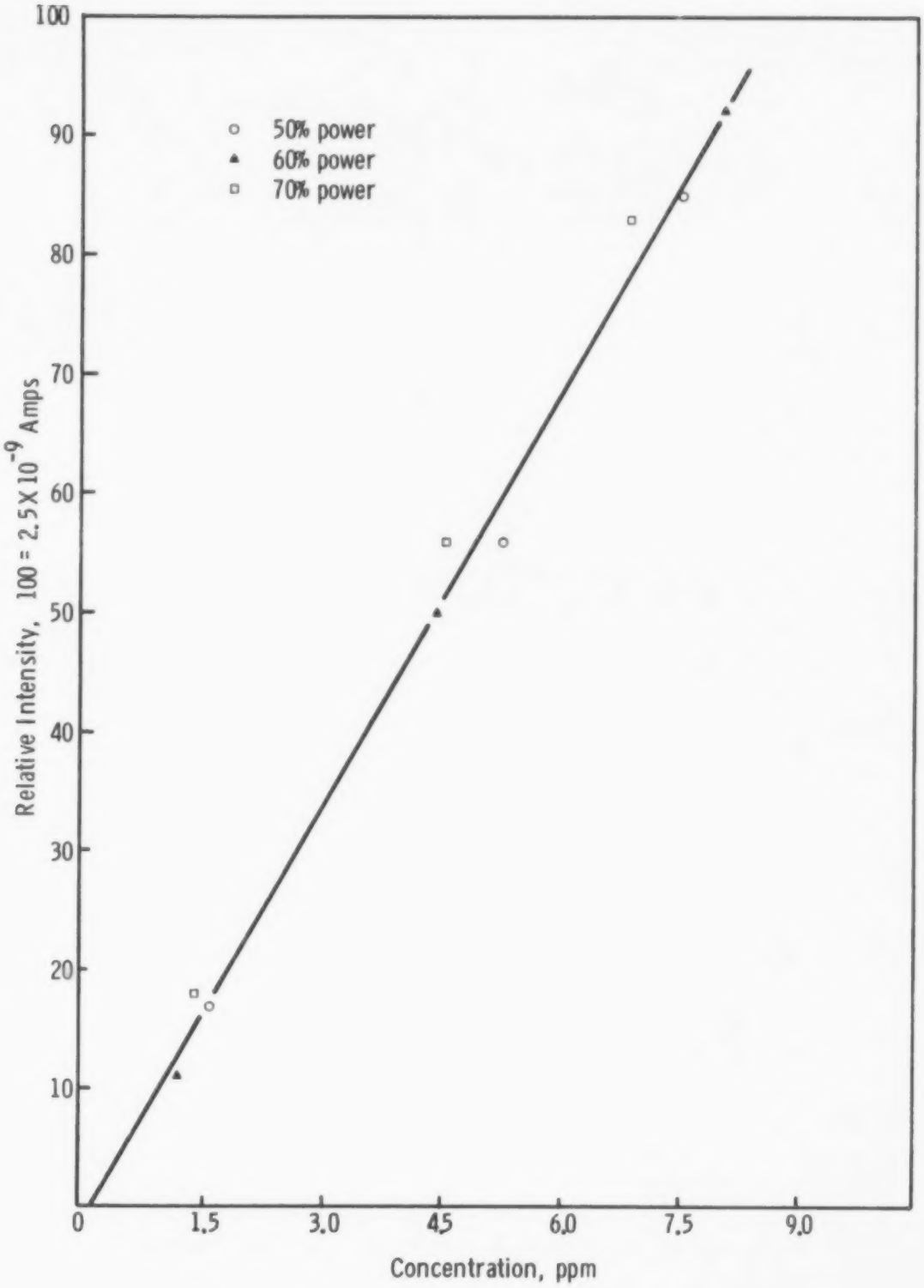


Figure 15. Influence of Microwave Power on Nitric Oxide Calibration.

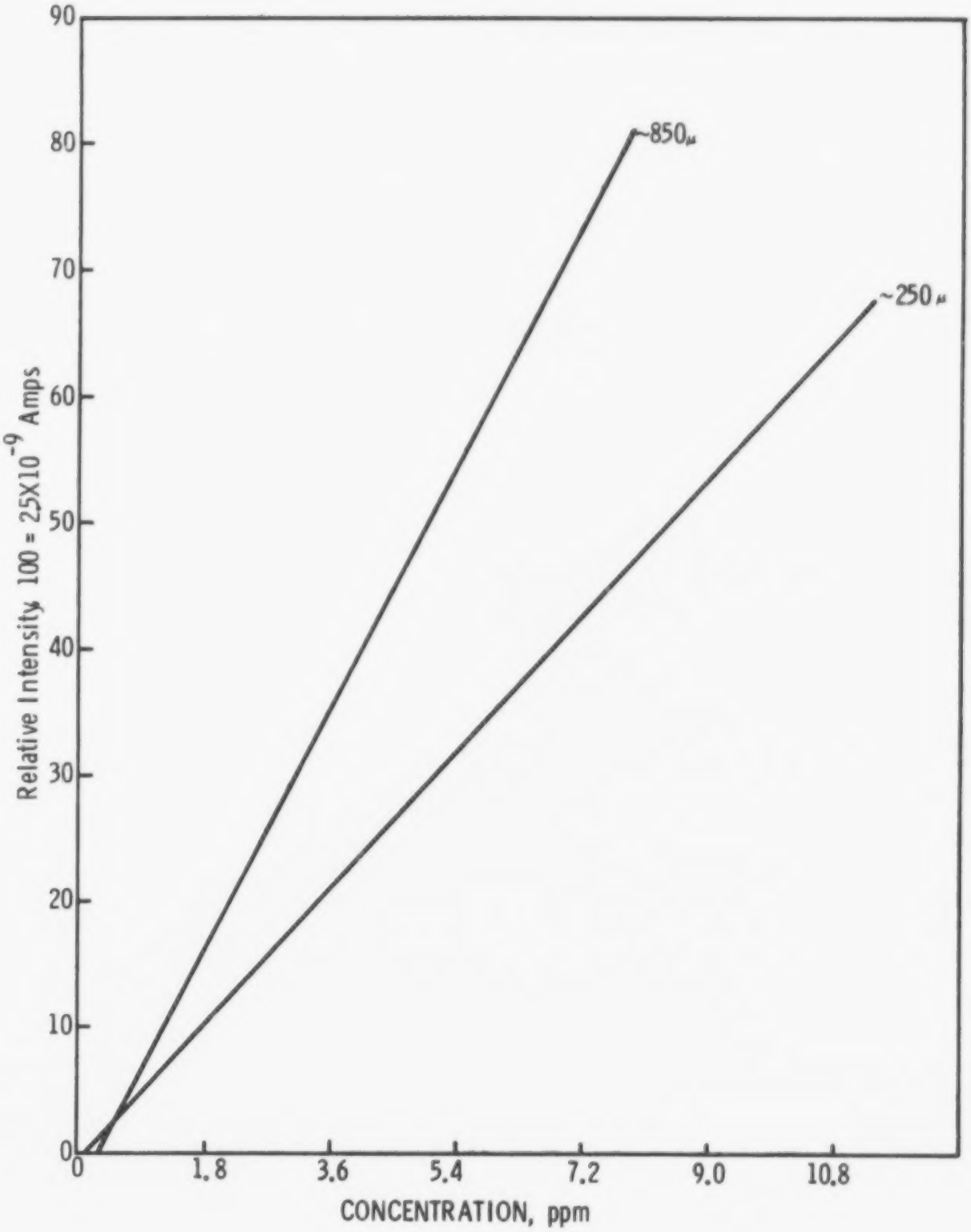


Figure 16. Pressure Dependence of the NO-O Reaction.

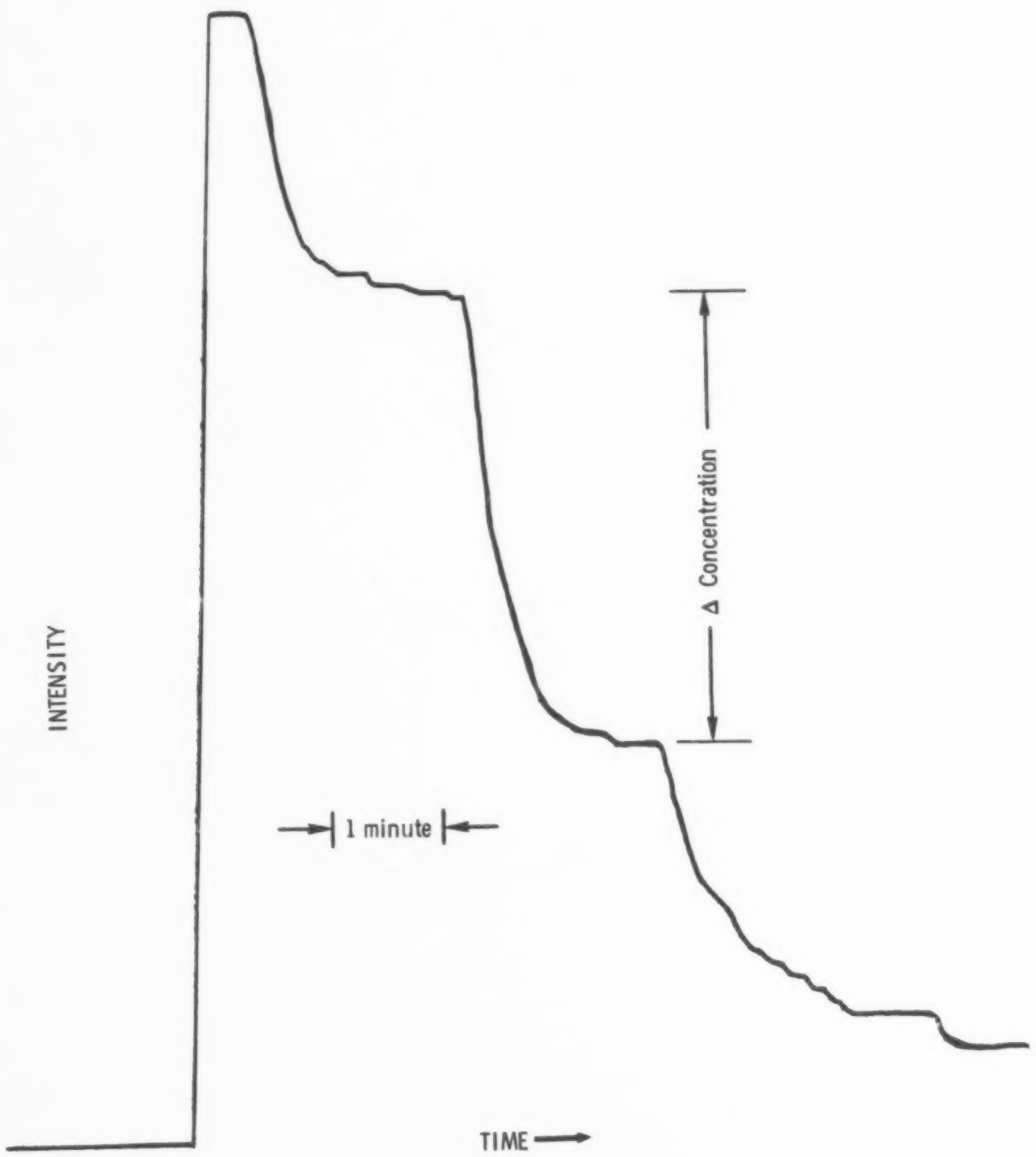


Figure 17. Time Response Characteristic of Nitric Oxide.

limit observed in this study was one-thousandth of the background intensity attests to the excellent operation of the mechanical chopper - lock-in voltmeter assembly. If a convenient means were available for purification of the oxygen input stream to the microwave cavity, much higher detection sensitivities would be expected.

6.2.3 The CO-O Chemiluminescent Glow

A very faint blue glow was observed in the spherical reaction chamber when additions of undiluted carbon monoxide were made. These additions, ranging from 1.5% to approximately 150 ppm in the chamber, gave intensity measurements much too low to predict good detection sensitivity for the CO-O reaction approach. Typical results are shown in Figure 18. These measurements were made under the same conditions and using the same operating parameters as in the case of NO-O. A Schott interference filter transmitting a 100 A band centered at 4560 A was employed to isolate the spectral region selected for detecting CO. Good linearity in response was obtained over the concentration range covered. The lowest measurement, corresponding to approximately 150 ppm, was somewhat questionable because only a slight variation in intensity above background was observed. Since the detection objective for the CO-O reaction covered a range of 0.5 to 50 ppm, the minimum detectable concentration obtained in this study indicated little possibility of achieving these objectives in the present system. Some improvement in system design might enhance detectability sufficiently to enable us to meet the minimum concentration limit stated above.

Considerable effort was spent attempting to improve sensitivity of the CO-O glow but insufficient time was available to adequately investigate all possible avenues which might lead to such improvement. A series of intensity measurements were made using no interference filter in the system but rather passing all radiation emanating from the reaction chamber. This approach showed little if any improvement in sensitivity due to the fact that background increased proportionately, detracting from any gain that may have resulted from the extended band passed onto the detector. A blocking filter passing all wavelengths below approximately 5000 A was tried but, again, sufficient improvement was not gained. Redesign of the reaction chamber coupled with a more optimum transfer of energy to the detector might offer a possible route to improvement. A reaction chamber similar to the one used for the spectral characterization study (Figure 6) would seem a logical starting point since a greater emitting volume could be observed.

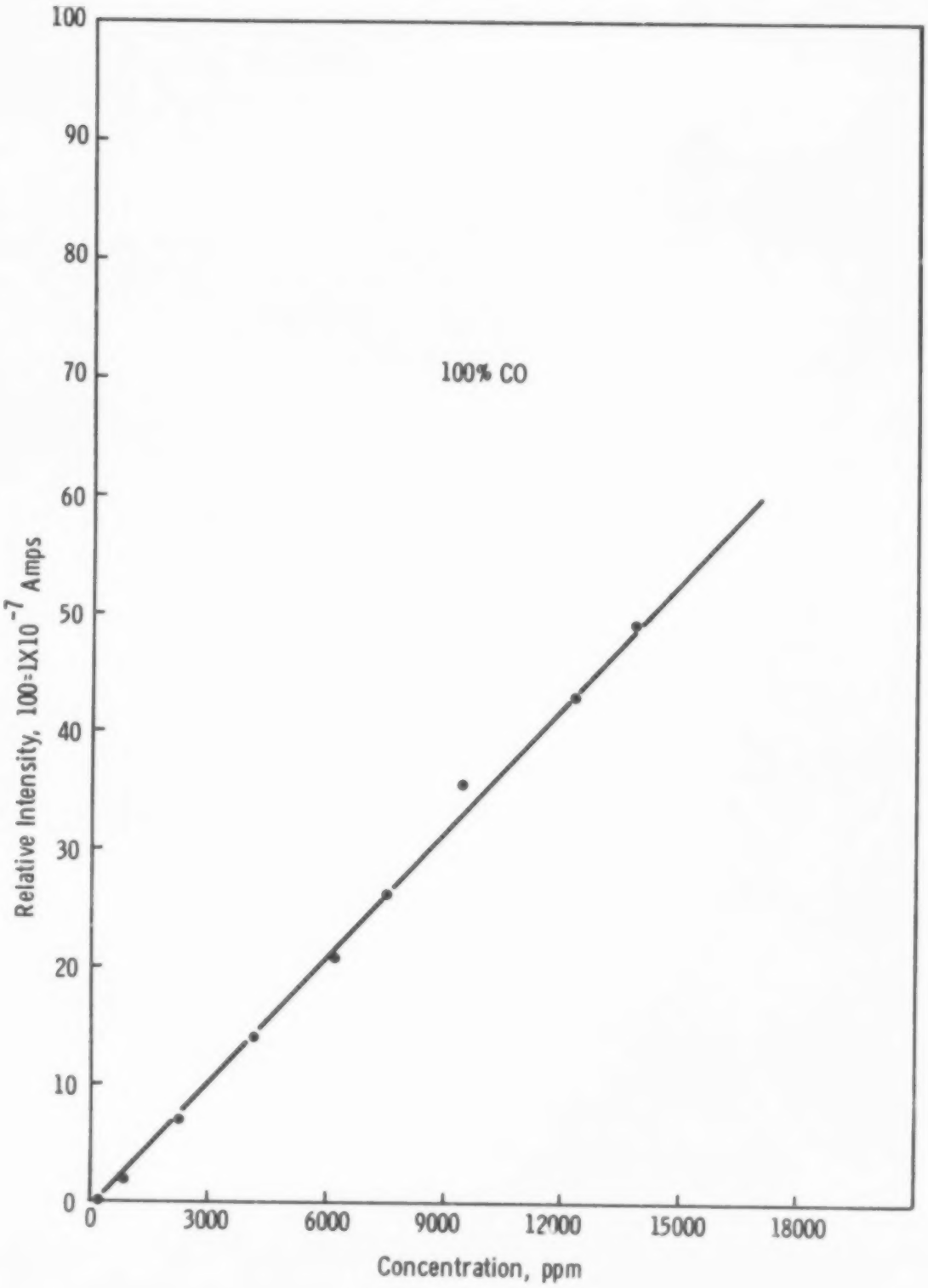


Figure 18. Calibration Curve for Carbon Monoxide.

6.2.4 The SO_2-O Chemiluminescent Glow

Studies of the chemiluminescent glow resulting from SO_2 addition to the spherical reactor were conducted employing either pure SO_2 or a 0.28% mixture of SO_2 in nitrogen. The reaction pressure was again maintained at 0.85 torr, the microwave cavity was run at 50% of power and the oxygen flow rate through the cavity was held constant at 330 cc/min (STP). In all but the last series of experiments, a Schott interference filter was used that had maximum transmission (30%) at 3510 A with half-width of 50 A.

Under these conditions the calibration curves shown in Figures 19 and 20 were obtained. Figure 19 demonstrates the linear response on addition of pure SO_2 to the reactor using the 0-5 cc/min Hastings-Raydist mass flowmeter. The range of SO_2 concentration covered in this calibration vary from 1.3% down to 3000 ppm. In Figure 20 the calibration curve obtained using the 0.28% SO_2 in nitrogen mixture is presented. The intensity was found to vary linearly with concentration in the range from 4.25 ppm to about 200 ppb. Under these conditions it appeared that a lower detection limit of 100 ppb SO_2 might be the limiting sensitivity.

An additional problem was observed during these calibration experiments. At high concentrations of SO_2, where low gain conditions were used in the detection system, the intensity rose sharply to a maximum when SO_2 flow was started and fell sharply to baseline when the flow was stopped. As the concentration was successively decreased, the rate of rise to constant maximum intensity and the rate of decay to baseline became very long (up to 30 minutes at the 200 ppb level). It appeared that adsorption of SO_2 on the reactor wall up to some saturation point was required before the full chemiluminescent glow at that specific concentration could be achieved. This interpretation was reinforced by observations that the decay rate after flow was stopped followed a mathematical form characteristic of desorption kinetics. The intensity data plotted in Figure 20 were obtained by establishing the flow conditions through the mass flowmeter and waiting until the glow intensity reached a constant value over a period of time. The reaction chamber was then run on the dissociated oxygen flow until the photocell again indicated baseline response before the next calibration point was determined.

During the last few days of this contract a UG-11 Schott filter was obtained. It transmits wavelengths in the region between 4000 and 2500 A, the peak transmission ($\sim$90%) occurring at 3250 A. A very limited study of the SO_2 chemiluminescent glow when this broad-band filter was substituted for the narrow-band pass filter indicated two effects. First, the measured

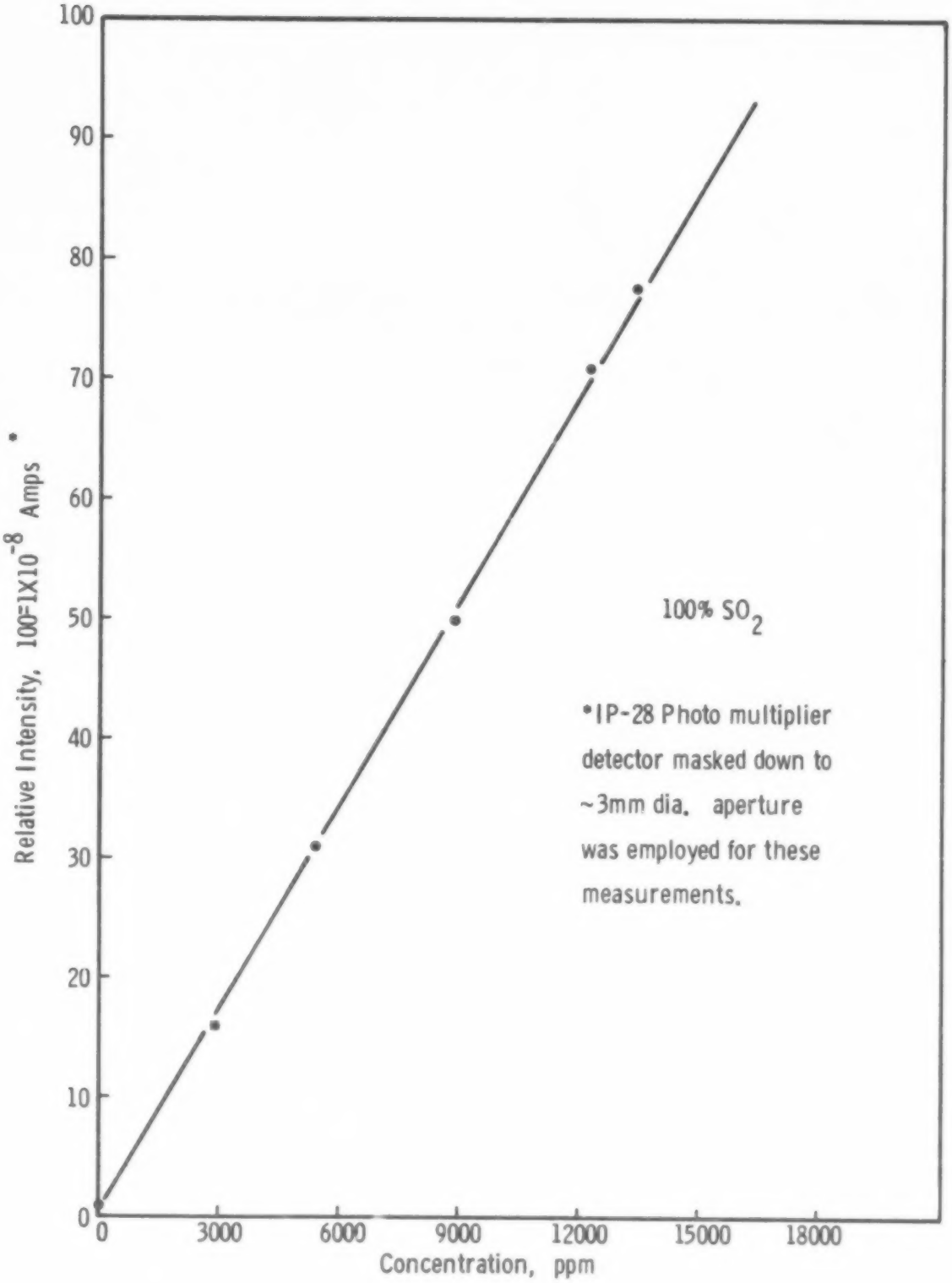


Figure 19. Calibration Curve for Sulfur Dioxide.

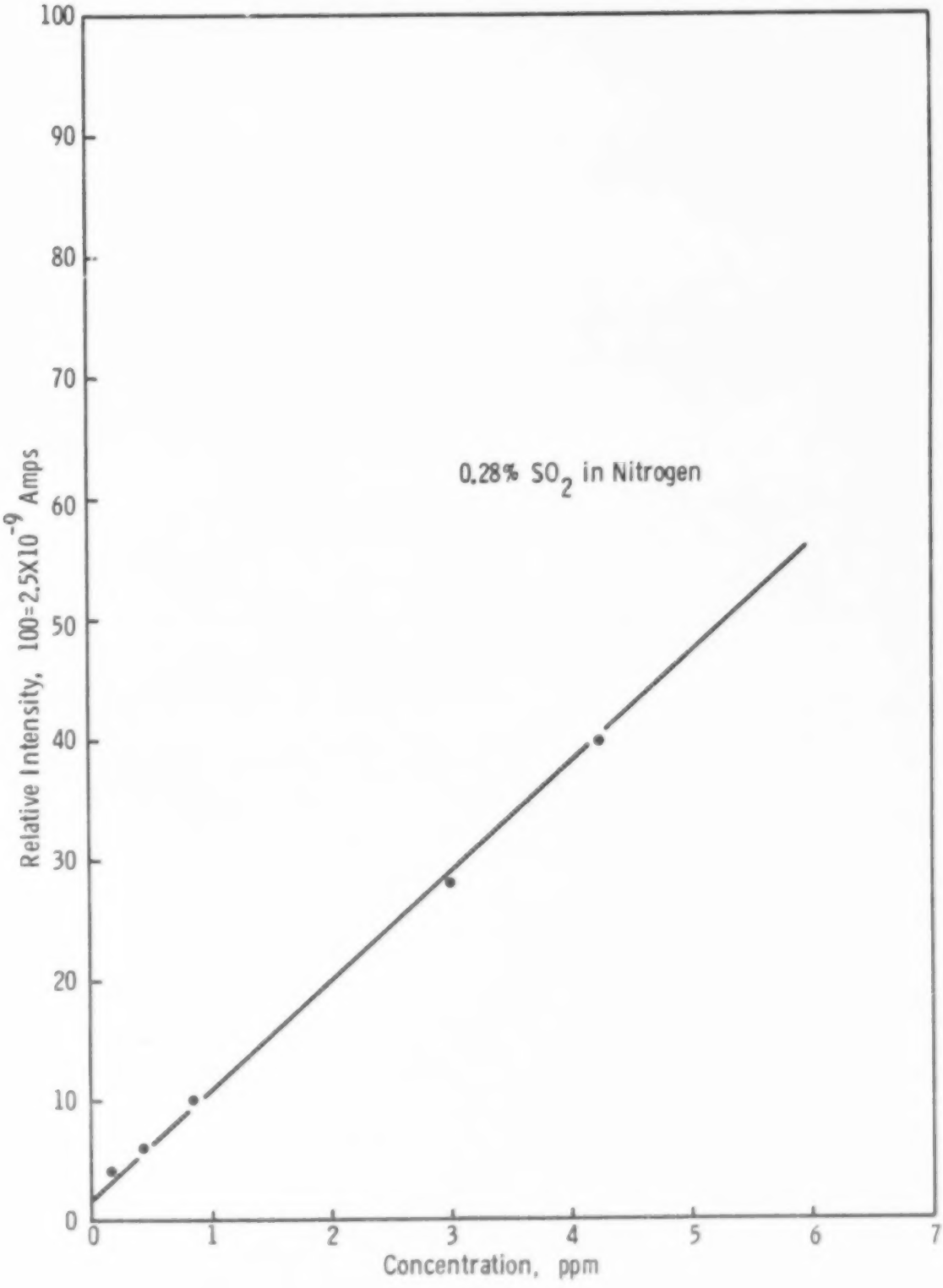


Figure 20. Calibration Curve for Sulfur Dioxide.

intensities of the SO_2 glow were increased on the average by a factor of 150. Second, under the low SO_2 concentration conditions, the response and decay times of the glow were much more rapid. The first observation decreases the estimate of minimum detection limit characteristic of this laboratory apparatus to 1 ppb. Table II presents comparative sensitivities of the SO_2 glow intensity for the two filters. The difference in response times of the SO_2 glow when the two filter systems were employed is illustrated in Figure 21. The rise time and decay times of the glow with the UG-11 filter are 0.6 and 2.15 minutes, respectively, instead of the 1/2-hour times experienced with the narrow-band pass filter.

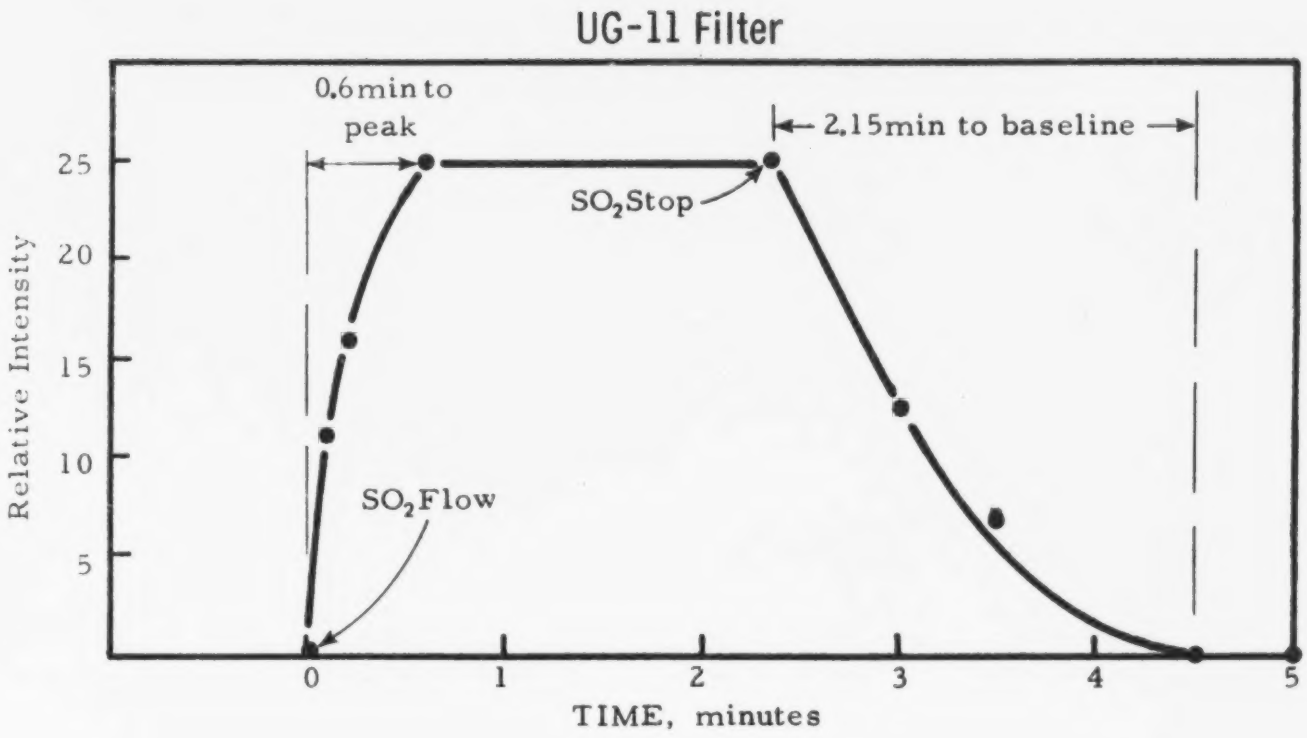
Table II

EXTENT OF INCREASED DETECTION CAPABILITY
FOR SO_2 CHEMILUMINESCENCE WITH BROAD BAND FILTER

SO_2 (ppb)	Current (amp)		Ratio
	Narrow-Band Filter	Broad-Band Filter	Broad Band/ Narrow Band
180	1.5×10^{-10}	2.5×10^{-8}	1.7×10^{2}
850	2.5×10^{-10}	3.7×10^{-8}	1.5×10^{2}

The reasons for this difference in behavior is not understood at this time. It could be that the weak glow centered about the wavelength of 3510 A results from a wall-catalyzed reaction while the more intense glow observed over the 4000-2500 A range may arise from a homogeneous gas phase reaction.

As is the case with the NO-O glow reaction, the 1 ppb lower limit of detection characteristic of the laboratory apparatus could be significantly reduced by further optimization of the system. Changes in reactor geometry and reactor-photomultiplier orientation would enhance the recorded emission intensity by increase in emitting volume and more optimum transfer of light into the sensitive area of the detector.



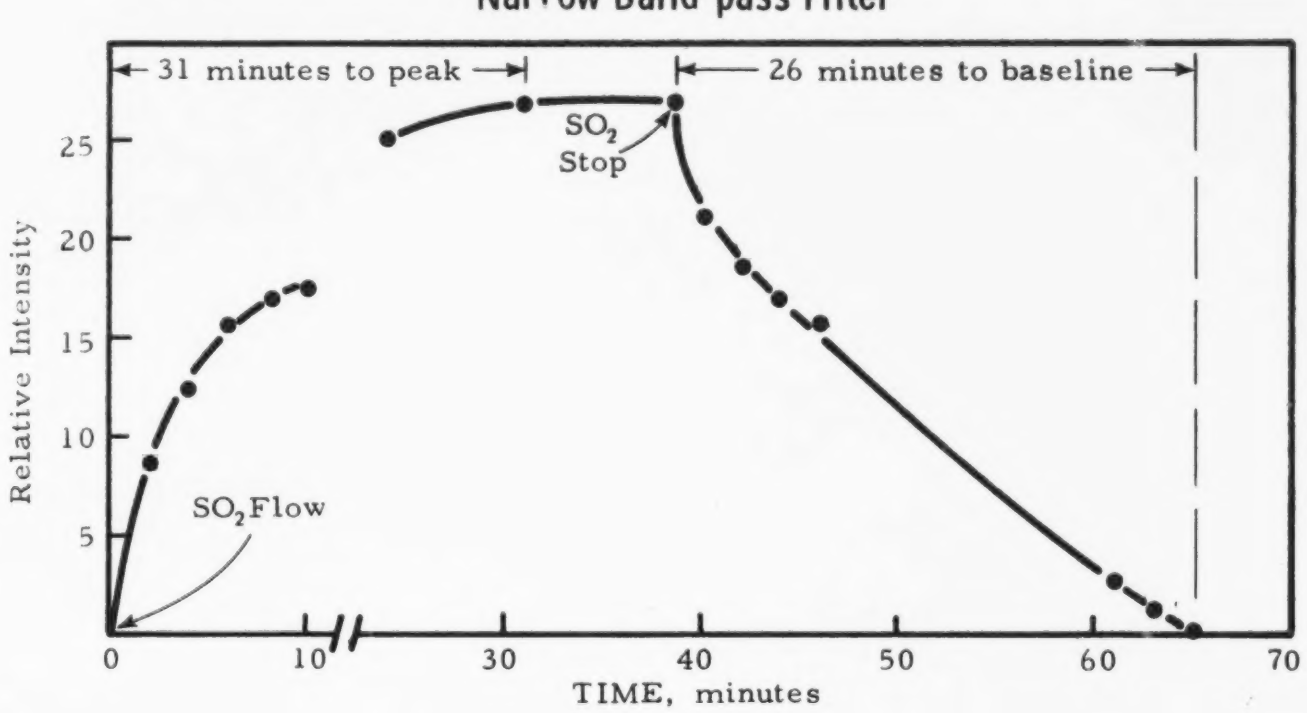


Figure 21. Time Response Characteristics of Sulfur Dioxide.

6.3 INTERFERENCE BY GASEOUS COMPONENTS COMMON TO POLLUTED AIR

Since the lower limits of detection for NO, CO, and SO_2 by chemiluminescent reactions were established (Section 6.2) under very idealized conditions, a study of the effects (if any) of other polluted air constituents on detection sensitivity was required to assess the applicability of the chemiluminescent approach to practical monitoring problems. For this program, five possible interfering components were studied: N_2O, CO_2, CH_3, H_2O, and NO_2.

Interference was determined by establishing a chemiluminescence glow in the spherical reaction chamber corresponding to 1 ppm of the pollutant understudy. The possible interfering agent was added to the flow stream entering the reaction chamber at a rate of 1 cc/min, which corresponded to a concentration of approximately 3000 ppm within the chamber. This concentration, with the exception of H_2O vapor, represents a minimum tenfold increase over the concentration found in ambient air (for the CO_2 case) to many thousand-fold increase over NO_2 under similar ambient conditions. In addition to the candidates listed above, interference effects by one pollutant on the others were studied in considerable detail. Results of these studies are listed in Table III.

Nitrogen dioxide, as shown in Table III, is the only case where interference was observed to any real and measurable extent. In this case, the responses of NO_2 (Figure 22) and NO are identical, both oxides showing linear glow intensity-concentration relationships and exhibiting identical curve slopes. Spectra of the chemiluminescent glow resulting from the reaction of NO_2 and atomic oxygen further substantiate this similarity. The chemiluminescent reaction involving the oxygen atom is therefore not selective for NO alone but still provides a sensitive means for detecting NO-NO_2 in ppb concentrations.

Table III

INTERFERENCE EFFECTS BY POLLUTANTS

Pollutant	Interfering Species							
	N_2O	CO_2	CH_3	H_2O	NO_2	NO	CO	SO_2
NO	No	No	No	No	Yes	--	No	No
CO	--	--	--	--	--	No	--	No
SO_2	No	No	No	No	No	No	No	--

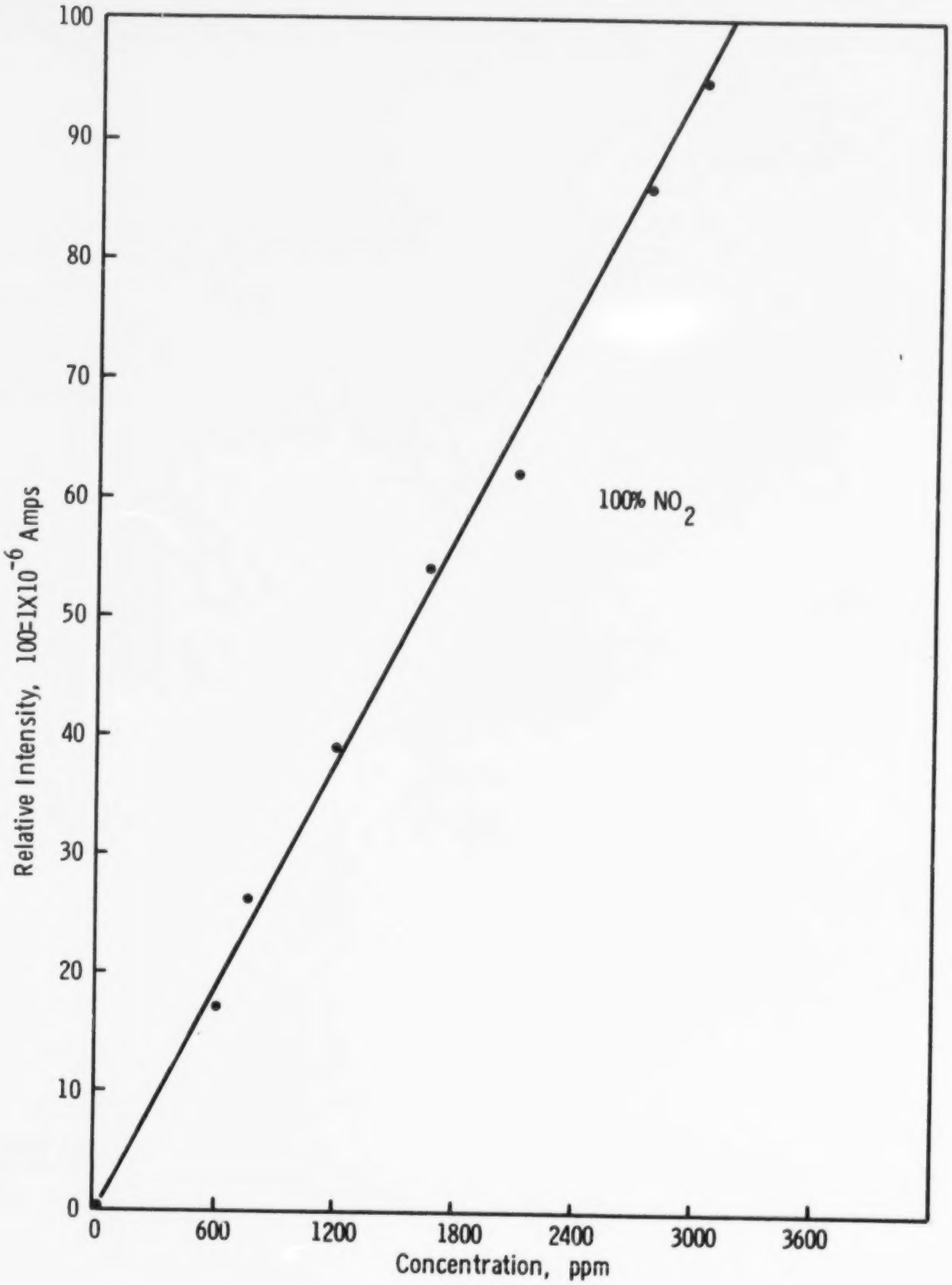


Figure 22. Calibration Curve for Nitrogen Dioxide.

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